SOME EXPERIMENTS ON THE PYROLYSIS OF TOLUENE

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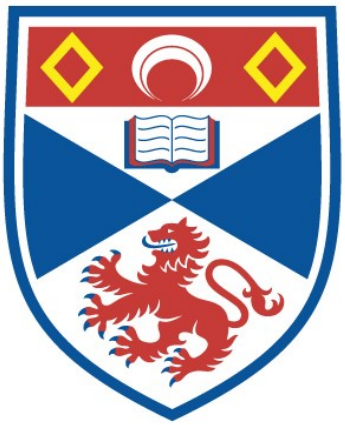
A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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SOME EXPERIMENTS ON

THE

PYROLYSIS OF TOLUENE.

A Thesis Presented

by

FRANCES GERALDINE SMITH

to the

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DECLARATION.

I hereby declare that the following Thesis is a record of results of experiments carried out by me, that it is my own composition, and that it has not previously been presented in application for a Higher Degree.

The experiments were carried out in the Chemistry Research Laboratories of St.Salvator's College, St.Andrews, under the supervision of Dr. C. Horrex.

CERTIFICATE.

I hereby certify that Frances Geraldine Smith was engaged upon research work for thirteen terms under my supervision; that she has fulfilled the conditions of Ordinance No.16 (St. Andrews), and is qualified to submit the accompanying Thesis in application for the degree of Doctor of Philosophy.

CAREER.

I entered the University of St. Andrews in 1949, and graduated in 1953 with Second Class Honours in Chemistry.

The work described in this Thesis was carried out under the direction of Dr. C. Horrex during the period August 1953 to September 1956.

ACKNOWLEDGEMENTS.

I should like to express my gratitude to Dr.C.Horrex for his help in the practical and theoretical aspects of this work, and to thank Professor John Read, F.R.S., for the provision of research facilities.

I am indebted to the Shell Petroleum Company Limited for a grant which enabled the first year of this research to be carried out, and to the Department of Scientific and Industrial Research for a Maintenance Allowance for the remaining two years.

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INTRODUCTION.

In the last ten years various methods have been applied to the determination of bond dissociation energies in organic molecules. While considerable success has been achieved it seems unrealistic to accept many of the values which are quoted until they have been derived by more than one method, and by more than one set of workers. A short survey of the field shows that most of the current values have been obtained by the application of one particular form of the chemical kinetic method, and that this has been done by one author and his collaborators.

The chemical kinetic method for bond dissociation energy determinations considers that the energy of activation of the gaseous thermal dissociation process:-

$$R\text{-}X \;=\; R\text{-} + \text{-}X \qquad (1)$$

can be determined under suitable conditions, and, assuming that the energy of activation for the reverse of (1) is zero, the energy of activation (E_1) for the forward process is equated to the endothermicity of the reaction. This produces the relationship

$$\begin{aligned} \Delta H(\text{reaction (1)}) &= \Delta H_f(R\text{-}) + \Delta H_f(X\text{-}) - \Delta H_f(R\text{-}X) \\ &= D(R\text{-}X) \\ &= E_1 \qquad (2) \end{aligned}$$

where D(R-X) is the value of the bond dissociation energy, and ΔH_f is the heat of formation of the specified entity in the gas phase. (We are ignoring here the difference between the enthalpy

and internal energy change in (1). In many instances the accuracy of the kinetically derived E_1 does not warrant any distinction.)

In 1948 Szwarc studied the pyrolysis of toluene, and obtained the value of 77.5 k.cal/mole for the energy of activation of the decomposition of toluene. He postulated as the rate determining step a first order process

$$C_6H_5CH_2\text{-}H \;=\; C_6H_5CH_2\text{-} \;+\; \text{-}H$$

where the bond broken was a side chain C-H bond, and considered the 77.5 k.cal./mole to be the dissociation energy of this bond. On the basis of previous work on the pyrolysis of benzyl iodide, and from general theoretical considerations, he suggested that the benzyl radical was stable, and that the hydrogen atoms were rapidly removed by a non-chain reaction with toluene. By using equation (2) and inserting the values for $\Delta H_f(H)$ and $\Delta H_f(C_6H_5CH_3)$ it became possible to deduce a value for $\Delta H_f(C_6H_5CH_2\text{-})$.

In further studies Szwarc pyrolysed various compounds R-X in the presence of excess toluene, arguing that reactive radicals or atoms would be quickly removed by the reaction

$$\underset{(\text{or } X\text{-})}{R\text{-}} \;+\; C_6H_5CH_2\text{-}H \;=\; \underset{(\text{or}(H\text{-}X))}{R\text{-}H} \;+\; C_6H_5CH_2\text{-} \qquad (3)$$

and the benzyl radicals produced would dimerise. Among the compounds R-X were benzyl bromide[2] and various substituted benzyl bromides,[3] and the dissociated bromine atoms were trapped as hydrogen bromide. From such pyrolyses of $C_6H_5CH_2$-X compounds Szwarc was able by use of equation (2) to obtain several separate

values of $\Delta H_f(C_6H_5CH_2-)$ with good general agreement between them. Ethyl benzene was also pyrolysed using this toluene carrier gas technique[4], and the value of $\Delta H_f(CH_3-)$ found by application of equation (2) was in agreement with $D(CH_3-H)$ determined by other methods.

These cross-checking experiments have resulted in wide acceptance of the values of D(R-X) determined by his techniques. Moreover, if $\Delta H_f(R-)$ and $\Delta H_f(X-)$ are believed to be known from separate pyrolyses of, say, X-Br and R-Br, and if $\Delta H_f(R-X)$ is known from calorimetry it is apparent from equation (2) that D(R-X) can be predicted. Thus, a few reliable values of heats of formation of radicals can lead, by combination in this way, to several bond dissociation energy values.

The above presents the salient claims and methods of Szwarc with respect to the construction of a system of such dissociation energy values. When his data are examined more closely and attempts made to relate his findings to those of other workers with other methods, the results are less convincing. At the time of the commencement of the experimental work described in the following pages, there was known to be a big discrepancy between the 77.5k.cal/ mole suggested by Szwarc for $D(C_6H_5CH_2-H)$ and the value of 89.5 k.cal./mole deduced by VanArtsdalen[5] from the kinetics of the bromination of toluene. Moreover, with $D(CH_3-H)$ known to the 101 - 102 k.cal./mole the value of 77.5

/k.cal./mole

k.cal./mole for $D(C_6H_5CH_2\text{-}H)$ gives a value of 24 for the resonance energy of the benzyl radical in contrast to theoretically calculated values ranging from 11 to 16 k.cal/mole. Even if we allow for the uncertainties in the latter the discrepancy seems surprisingly high.

A study of the experimental evidence on toluene pyrolysis given by Szwarc shows several doubtful features. In particular he found it necessary to postulate a reaction

$$C_6H_5CH_3 + H\text{-} = CH_4 + C_6H_5\text{-} \qquad (4)$$

or

$$= CH_3 + C_6H_6 \qquad (5)$$

in order to account for a high proportion of methane in his gaseous products. Such breakdowns of the carbon skeleton of a hydrocarbon by the attack of free atoms are far from usual since extraction of peripheral atoms is normally predicted.

In view of the importance of accurate values of bond dissociation energies for chemical theory it was decided to re-investigate the pyrolysis of toluene using more extensive analytical techniques and experimental arrangements which might give a closer control of the kinetic behaviour of the reaction.

While the work was in progress the results of other pyrolytic investigations were published[6,7] by workers who had also been attracted by the difficulties of the position; some relevant electron impact data became available,[8,9,10] and two separate lines of investigation within the St. Andrews laboratories provided

supplementary evidence on the heat of formation of the benzyl radical.[11,12].

Before giving an account of the experimental work on toluene, a survey is given of the different lines of evidence for the value of $D(C_6H_5CH_2-H)$. The interest of the problem is such that all the applicable and known techniques have been applied to it.

There is a further general interest in a re-investigation of the pyrolysis. Szwarc has studied a large number of pyrolytic reactions, and has claimed that they obey a first order rate law with the temperature variation of the velocity constants (k) being given by:-

$$k = A.\exp.^{-E/RT}$$

where A is about 10^{13} and E is the relevant bond dissociation energy. In various cases he has assumed this value for A in the face of conflicting experimental evidence,[13,14]. arguing that it is the normal value for first order bond fissions. The results of this work, and of some of the other re-investigations mentioned throw doubts on his kinetic analysis and hence on his claimed normal A factor.

SURVEY OF PUBLISHED PYROLYTIC DATA ON TOLUENE AND OTHER DETERMINATIONS OF $D(C_6H_5CH_2\text{-}H)$.

In the previous pages, the state of knowledge of the toluene pyrolysis, and the intimately connected problem of the value of $D(C_6H_5CH_2\text{-}H)$ and $\Delta H_f(C_6H_5CH_2\text{-})$, has been outlined very briefly in order to indicate the general reasons for undertaking the work to be described in later pages. In this section an account is given of details of published work which are significant for this work, concentrating on the investigations which aimed at determining $D(C_6H_5CH_2\text{-}H)$, but reserving the discussion and comparison with the results of this thesis until after the latter have been presented.

Early Pyrolytic Work.

An early study of the products formed when toluene was passed through a heated tube was made by Graebe,[15] and in connection with later work it is interesting to note that among the substances he identified were anthracene, phenanthrene, diphenyl and dimethyldiphenyls.

Reaction mechanism studies on toluene before 1947 were few in number. Jost and Muffling[16] added mercurydimethyl to decomposing toluene and found no increase in rate at 690°C, and argued that the decomposition was not of a chain character. Hein and Mésee[17] added mercury vapour to decomposing toluene and isolated mercurydibenzyl and hydrogen among other products, and suggested a primary rupture of a side chain C-H bond in both these investigations.

Pyrolytic Work of Szwarc.

When Szwarc[1] took up this problem he decided to work at low percentage decompositions in order to minimise side reactions, and restricted his experiments to 0.01% to 1.1% decomposition. The technique was a flow method using reactant pressures ranging from 2.7 - 15.7mm.Hg. The text of the paper suggests that the range of temperature investigated was 680 - 850°C, whereas the numerical data show the range to be 738 - 864°C. The times of contact of the reactant with the hot zone were 0.235 - 0.905 seconds. The rate of reaction was followed by isolating the gas not liquified at -180°C, combusting the hydrogen over cupric oxide and noting the loss in pressure, and then considering as methane the residual gas not removed by the combustion conditions chosen. A test for the presence of C_2- hydrocarbons was made, but merely consisted of changing a -180°C bath on the product trap for one at -80°C and looking for a pressure rise. None was observed. Unless the (H_2 + CH_4) was removed first - and this is not stated - a pressure rise due to temperature change ought to have been observed. In any case, with low percentages of decomposition the solubility of C_2- hydrocarbons in the excess of liquid products and unchanged reactant would be a serious error.

The observed products were said to be hydrogen, methane, dibenzyl and benzene. A solid product is, of course, readily separated at the furnace exit in these reaction systems, and a

recrystallisation could provide dibenzyl for the melting point and mixed melting point which were obtained. But this does not permit the assertions made that all such product was dibenzyl or that it was present in the proportion of one mole per mole of gaseous product. No method whatever is given for the delicate quantitative analysis which would be required to determine quantities of dibenzyl on the milligram scale. Even less evidence is provided for the benzene. With less than 1% of this mixed with the undecomposed toluene, the task of analysis is formidable with present day resources of mass spectrometry and infra red spectrophotometry. The author is informed by Dr. Horrex that these techniques were not available in the Manchester University laboratories at the time - and gas chromatography had, of course, not been developed.

Szwarc suggested that his evidence supported a mechanism:-

$$C_6H_5CH_3 = C_6H_5CH_2^- + H^- \quad \text{(Rate determining)} \quad (1)$$

$$H^- + C_6H_5CH_3 = C_6H_6 + CH_3^- \quad (2)$$

$$H^- + C_6H_5CH_3 = C_6H_5CH_2^- + H_2 \quad (3)$$

$$CH_3^- + C_6H_5CH_3 = CH_4 + C_6H_5CH_2^- \quad (4)$$

$$2C_6H_5CH_2^- = C_6H_5CH_2CH_2C_6H_5 \quad (5)$$

This gives an overall stoichiometry based on combining

$$2C_6H_5CH_3 = C_6H_5CH_2CH_2C_6H_5 + H_2 \quad (6)$$

and

$$3C_6H_5CH_3 = C_6H_5CH_2CH_2C_6H_5 + C_6H_6 + CH_4 \quad (7)$$

in the proportions of the hydrogen to methane ratio in the gaseous products.

When we consider the presented kinetic results in detail only twenty-seven experiments in all are used for characterisation of the reaction kinetics, and twenty-four of these feature on the Arrhenius plot for the temperature variation of the velocity constant. The temperature control was not good, and makes it difficult to see the effects of variation of contact time and concentration of reactants. The data for these purposes are meagre, and it cannot be said that the variations were made independently of one another. For example, the effect of a pressure decrease was considered to have been tested in the following:-

Experiment No.	^{o}C	Pressure of toluene in mm.Hg.	Time of contact (seconds)	$k.sec^{-1}.10^{2}$
77	771	6.1	0.235	0.142
82	773	2.7	0.380	0.158

But with a fall in contact time for experiment 77 to 62% of the figure for experiment 82, the argument for the establishment of first order constants as being valid for this reaction is not well founded. Only three such pairs are given to examine concentration variations - and they are all at different temperatures. Similarly there are only two such pairs for

studying the effect of the variation of contact time. In three experiments the surface was increased by fifteen times. While the effect on reaction rate was definitely not proportionate, it is difficult to assess if any effect existed since appropriate blank experiments are not available.

When we consider the temperature coefficient of the first order constants which were calculated, it has been stated that the experiments reported at the lowest temperatures were not plotted on the graph of log.k against $1/T^{o}K$, since it was felt that loss of products occurred due to the minute amounts being handled. If these experiments are included, Bateman[18] has shown that the derived energy of activation would be 80 $\pm$ 4.2 k.cal./mole instead of the 77.5 $\pm$ 1.3 k.cal./mole which was claimed.

In spite of this later disclosure, the paper of 1948 actually used the values of the velocity constants at the lowest temperatures for a comparison of the activation energy for the toluene pyrolysis with that for each of the xylenes. Using the idea of a temperature independent factor of (2.0×10^{13}) $sec.^{-1}$ per methyl group, the velocity constants at the lowest temperatures of experiment were converted into comparable energies of activation. It seems surprising that if these results had to be discarded for an Arrhenius plot to deduce the energy of activation, they can be used in a later paragraph for a more arbitary method of deriving this quantity.

Although this piece of work is clearly open to much

detailed criticism, the derived result for $D(C_6H_5CH_2-H)$ = 77.5 k.cal./mole has presumably survived in scientific esteem because of the claimed agreement between it and various dissociation energies for $C_6H_5CH_2-X$ compounds. This point will be discussed later.

Pyrolytic Work of Blades, Blades and Steacie.

A few years later, and during the course of the experimental work of this thesis, details of the re-investigation of the pyrolysis of toluene were published from the National Research Council laboratories in Ottawa. In this work, the main effort was devoted to establishing the nature of the products formed during the pyrolysis, although some kinetic data was also obtained.

The intention of Steacie et al. was to repeat the method and experimental conditions used by Szwarc, but it is important to notice that they made some serious alterations, and in some matters have reported their work in a surprisingly inadequate fashion. Whereas Szwarc's experiments lay between 730 - 864°C, the range of temperatures used by Steacie et al. has to be deduced from the log. k versus $1/T°K$ graph presented in the paper - their Fig.6. The range appears to be 858 - 947°C, thus the lowest temperature used by these workers is only six degrees below the highest temperature used by Szwarc. In one table of results experiments appear to have been performed at 848°C, but there are serious omissions in the

paper of the precise temperature and other experimental conditions used to prepare the products of pyrolysis which were then subjected to extensive analytical investigation. Some of the methods adopted in the analyses used substantial amounts of material, a one gram sample of the non-volatile fraction is mentioned, and it seems quite possible that in order to obtain such large amounts the higher regions of their temperature range were used. It is quite conceivable that the character of the reactions proceeding could be substantially altered in these circumstances.

The other material variation from Szwarc's conditions lies in the time of contact used for the determination of the temperature dependence of the velocity constant, which was 0.068 second, this being about a quarter of the lowest value used by Szwarc. In relation to the dimensions of the reactor, 1.7 x 84cm., which was used, it is questionable whether temperature equilibrium with the wall was reached.

In the matter of the products of the pyrolysis, Steacie's investigation confirmed the existence of the major products claimed by Szwarc, disclosed the presence of other liquid and solid products, and showed some differences on proportions of materials. Steacie et al. stated that the gaseous products consisted of 69% hydrogen and 31% methane as compared with Szwarc's value H_2 : CH_4 = 60 : 40; and C_2-hydrocarbons were not detected when prepyrolysed toluene was used.

In the liquid products benzene was separated by fractional distillation and characterised; the amount was approximately equal to that of the methane found. Also there was spectrophotometric evidence for styrene in the higher boiling liquid products, and this was estimated to be one-eighth of the benzene formed.

In contrast to Szwarc, who claimed that the solid product was dibenzyl, Steacie et al. found the non-volatile materials to be an oil with a strong ultra-violet absorption, and a carbon : hydrogen ratio of unity. This led them to consider dimethyldiphenyls as possible constituents, and they produced convincing evidence for this view. By oxidation procedures diphenic acid was isolated, and chromatographic separations led them to suggest mixtures of the dimethyldiphenyl isomers. As far as dibenzyl was concerned, they concluded it might be not more than 50% of the non-volatile material.

For their kinetic work they used the total of the hydrogen and methane produced as an index of the reaction rate. They were unable to confirm the first order character of the decomposition which had been claimed, and stated that a calculated first order constant **rises** by a factor of two when the contact time increases by a factor of six. The only data produced for the effect of varying concentration is, unfortunately, complicated by an accompanying variation in contact time, in the same way as in Szwarc's work.

Tests were also made of the effect of packing the reaction vessel, and they found surface conditions affected the rate, in particular a difference was noted between a clean reaction vessel and one which had been used previously.

Although Steacie et al. did not consider a first order law to be adequately obeyed by this pyrolysis, they pointed out that their plot of log. (calculated first order constant) against $1/T^{\circ}K$ would give an energy of activation of about 90K.cal./mole in contrast to the value 77.5 k.cal./mole obtained by Szwarc.

In an appendix to this paper on the pyrolysis of toluene, Steacie et al. gave some data for the pyrolysis of dibenzyl in the presence of toluene using the same reaction technique as for the toluene pyrolysis, and a temperature range 825 - $897^{\circ}C$.

Their stated purpose was to discover the source of formation of the dimethyldiphenyls observed as products of the pyrolysis of toluene. On the basis of a high ultra-violet absorption for the products, they decided that the more dibenzyl there was present the greater was the amount of dimethyldiphenyls that was formed. The amount of dimethyldiphenyl compounds rose substantially over the temperature range investigated, and it was shown that dibenzyl alone could yield these materials. Their meagre data did not permit them to reach any conclusion about the origin of

these compounds.

They did observe the production of considerable amounts of hydrogen from the pyrolysis of mixtures of dibenzyl and toluene, but this was not accompanied by any increase in the methane production, and they concluded that this casts some doubt on the feasibility of the reaction:-

$$H\cdot + C_6H_5CH_3 = C_6H_6 + CH_3\cdot \qquad (2)$$

In connection with this work on dibenzyl and toluene it seems reasonable to draw attention to data which is available on the rate of the decomposition of dibenzyl. This was studied by Norrex and Miles[19], and their work was revised by Pittilo[11], who also used flow techniques with short contact times comparable to Steacie's, but with a maximum temperature of 716°C. From their data, Steacie's operating temperature of 897°C gives a very high rate of decomposition for dibenzyl. In the one blank experiment on dibenzyl alone which is quoted by Steacie, a loss of 40% of the dibenzyl is recorded. The lower temperature work at St. Andrews produced no significant amount of hydrogen, whereas Steacie et al. record 15.5 mole% calculated on the dibenzyl. It seems that their conditions may have caused considerable cracking of the dibenzyl molecule, which could be the origin of some of their products.

In a later note, Blades and Steacie[20] conducted some more illuminating experiments on the problem of whether hydrogen atoms reacting with toluene can produce removal of the methyl

group. n-Propylbenzene was decomposed in the presence of a forty fold excess of deuterated toluene, the deuterium being in the side chain. The temperature used was 722°C and, in the flow system used, this would not cause decomposition of the toluene.

Szwarc[21] had done similar work with normal toluene, and suggested a mechanism on the following lines:-

$$C_6H_5C_3H_7 = C_6H_5CH_2\text{-} + C_2H_5\text{-} \quad (8)$$

$$C_2H_5\text{-} = C_2H_4 + H\text{-} \quad (9)$$

$$H\text{-} + C_6H_5CH_3 = C_6H_5CH_2\text{-} + H_2 \quad (10)$$

$$H\text{-} + 2C_6H_5CH_3 = C_6H_5CH_2\text{-} + CH_4 + C_6H_6 \quad (11)$$

Steacie found the same products as Szwarc; hydrogen, methane, ethane, ethylene, benzene and dibenzyl; the methane had the isotopic constitution:-

$$CD_4 : CD_3H ; CD_2H_2 = 1 : 1.5 : 1,$$

the benzene was largely C_6H_6, and the hydrogen an equal mixture of H_2 and HD. The hydrogen to methane ratio was roughly the same as in the pyrolysis of toluene alone.

As a result of these findings, Steacie reversed his view expressed on page 15 on the existence of the total reaction expressed in (11), and from the isotopic constitution of his materials he concluded that (11) occurred in the stages:-

$$H^- + C_6H_5CD_3 = CD_3^- + C_6H_6 \qquad (11a)$$

$$CD_3^- + C_6H_5CD_3 = CD_4 + C_6H_5CD_2^- \qquad (11b)$$

The isotopic compositions of the methanes were ascribed to the original deuterated toluene having the composition 66% d_5, 29% d_2 and 5% d_1. To account for the high proportion of H_2 in relation to HD, Steacie suggested that abstraction of hydrogen atoms from the ring system can take place. This ignores the fact that the (C - α H) bond in n-propylbenzene should be weaker than the side chain (C - H) bond in toluene by 5 - 6 k.cal/mole, because it is a secondary hydrogen bond, and this would go a long way to annulling the forty fold difference in the concentrations of toluene and n-propylbenzene which existed in their experiments.

Pyrolytic Work of Genco, Duke, Griffel and Jennings.

A recent technical information bulletin of the United States Atomic Energy Commission[7] contains the results of sixteen experiments on the pyrolysis of toluene in an apparatus similar to that used by Szwarc and operated at similar pressures and contact times. With such a small range of experiments it was clearly impossible for the authors to settle some of the difficult points in this problem, for example, there was no attempt at justifying the application of a first order kinetic law.

The deposition of a layer of carbon was noted in some of their runs, but it was concluded that this had very little

effect on the rate of the reaction. Their temperature range of 703 - 819°C was effectively 30° less at each limit than that used by Szwarc. As a result they quote percentages of decomposition as low as 3.77×10^{-5}%, and their maximum value is only 0.196%.

With regard to the proportions of products, they claimed one new feature - that the gases contained a somewhat higher proportion of methane at the lower temperatures, the range being from 36% at 819°C to 42% at 705°C. In contrast to Szwarc and Steacie et al., small but unestimated amounts of ethylene, propylene and propyne were observed. There is no evidence of an analysis for benzene and although the solid product was weighed and found to be approximately equal to the methane formed, the sole treatment of the qualitative analysis consists of an ultra-violet absorption spectrum having the rough shape of that for a diphenyl compound with the inflections of dibenzyl superimposed.

By using calculated first order constants, and ignoring four runs with toluene which was not prepyrolysed, they deduced a value for the activation energy of about 84 k.cal./mole. If the four omitted runs, actually at the highest temperatures, are included, their value is 78.3 k.cal./mole. The order of magnitude of their velocity constants agrees with those quoted by Szwarc.

TABLE I

X	$\Delta H_f(C_6H_5CH_2-X)$	$D(C_6H_5CH_2-X)$	$\Delta H_f(X-)$	$\Delta H_f(X-)$ other sources.	Ref.
CH_3	7.1	83.2 ± 1.5	32.7	32.1	4
C_2H_5	1.9	57.5 ± 4	22 ± 4	25.3	21
Br	15.6 ± 3	50.5 ± 2	28.7 ± 4	22.7	2
NH_2	14.0 ± 3	59.4	35.5 ± 5	41.0	22

$$\Delta H_f(X-)_{\text{column (4)}} = D(C_6H_5CH_2-H) - \Delta H_f(C_6H_5CH_2-) + \Delta H_f(C_6H_5CH_2-X)$$

where $\Delta H_f(C_6H_5CH_2-) = 37.2$ k.cal./mole.

Pyrolytic Work on $C_6H_5CH_2$-X Compounds.

Pyrolytic work in the presence of toluene on $C_6H_5CH_2$-X compounds, where X = CH_3, C_2H_5, Br, NH_2, etc., has provided a value of the dissociation energy $D(C_6H_5CH_2-X)$ in the compound used, which in combination with the heat of formation of the benzyl radical obtained from Szwarc's value for the dissociation energy $D(C_6H_5CH_2-H)$ enables a value for the heat of formation of the radical X to be deduced using equation (2) page (1). The data used are all due to Szwarc and collaborators, and the examples given in Table I can be quoted as a justification of his general scheme of bond dissociation energies.

In detail, the method consists of applying the flow technique using some 8 - 15 mm. toluene, a partial pressure of $C_6H_5CH_2X$ in the region 0.01 - 1.00 mm., and contact times of the order 0.2 - 1.0 second. It is assumed that the initial dissociation:-

$$C_6H_5CH_2X \rightarrow C_6H_5CH_2\cdot + X\cdot$$

is followed by a fast reaction

$$X\cdot + C_6H_5CH_3 \rightarrow HX + C_6H_5CH_2\cdot$$

thus preventing chain reactions or other secondary complications.

The rate of reaction was followed by determining the amount of HX by appropriate methods such as titration, for example, in the case of hydrogen bromide, pressure measurement

and combustion in the case of methane. In all the mentioned pyrolyses the temperature independent factor was approximately 10^{13} second^{-1}.

Within the admitted uncertainty of some of the heats of formation used, the results of Table I seem to be a convincing justification for Szwarc's contentions. It should be noted that in several instances[2], there is an induced decomposition of toluene providing hydrogen and methane which accompany the formation of HX. Szwarc has suggested that this indicates the presence of free hydrogen atoms which might arise by the attack of X on dibenzyl followed by the decomposition of the radical $C_6H_5CH_2CHC_6H_5$ to stilbene.

$$X\cdot + C_6H_5CH_2CH_2C_6H_5 = C_6H_5CH_2CHC_6H_5 + H\text{-}X$$

$$C_6H_5CH_2CHC_6H_5 = C_6H_5CH{=}CHC_6H_5 + H\cdot$$

Such hydrogen atoms might attack the $C_6H_5CH_2X$ molecule also.

In view of the uncertainty about the value of $D(C_6H_5CH_2\text{-}H)$, it was thought desirable to repeat the decomposition of benzylbromide. Using a flow technique with nitrogen as the carrier gas and lower pressures of toluene then those used by Szwarc, Mearns[23] in the St.Andrews laboratories, has obtained adequate confirmation of a first order law under his conditions, but assesses $D(C_6H_5CH_2\text{-}Br)$ to be 58 k.cal./mole in contrast to Szwarc's value of 51 k.cal./mole.

Since Mearns' velocity constants at any temperature

are of the same order as those found by Szwarc, his temperature independent factor proves to be 1.5×10^{15} second^{-1}. This is the only repetition of any of the significant $C_6H_5CH_2X$ pyrolyses to be performed, and it is important to notice that it would only be consistent with a value of $D(C_6H_5CH_2-H)$ which is significantly higher than the value determined by Szwarc[2].

A particular case of the pyrolysis of a $C_6H_5CH_2X$ compound which is of interest is when $X = C_6H_5CH_2-$, in other words, the pyrolysis of dibenzyl. The central bond in this compound should be weaker than an ordinary (C - C) bond by twice the resonance energy of a single benzyl radical. Consequently, a determination of $D(C_6H_5CH_2 - CH_2C_6H_5)$ should facilitate a decision between the possible values for the heat of formation of the benzyl radical, and hence between the possible values for the bond dissociation energy in toluene $D(C_6H_5CH_2 - H)$.

The first study of the decomposition of dibenzyl was by Horrex and Miles[19] who deduced first order velocity constants represented by the equation:-

$$k \text{ sec.}^{-1} = 10^{9.5} \exp.^{-48000/RT}$$

and assumed that the products, toluene, benzene, styrene and stilbene, were the result of initially formed benzyl radicals attacking the parent molecule. While this energy of activation was in good agreement with $D(C_6H_5CH_2-H) = 77.5$k.cal./mole,

the temperature independent factor $10^{9.5}$ is most unusual for a first order decomposition.

The work was repeated by Pittilo[11] in St.Andrews using better analytical techniques. He decided that the products were correct but that the stoichiometry changed with concentration, and that the kinetic order for the formation of toluene was nearer 1.4 than unity. This suggested that a preliminary dissociation equilibrium existed:-

$$C_6H_5CH_2CH_2C_6H_5 \rightleftharpoons 2\ C_6H_5CH_2\cdot$$

and that only a few of the radicals attacked the parent molecule. This scheme would provide 1.5 order kinetics for toluene formation, and he demonstrated that ample benzyl radicals were available at the temperature of his pyrolytic work by adding fluorene and getting substantial increases in the amount of toluene produced. Fluorene is known to have a weakly bonded hydrogen atom.

From this starting point it seemed that if a mixture of $C_6H_5CH_2CH_2C_6H_5$ molecular weight 182 and $C_6H_5CD_2CD_2C_6H_5$ molecular weight 186 was heated appropriately, the formation of $C_6H_5CH_2CD_2C_6H_5$ molecular weight 184 would occur. Davidson[34], in St. Andrews, has carried out this reaction at pressures of the order of 1 mm. and followed the growth of the $C_6H_5CH_2CD_2C_6H_5$ by mass spectrometry.

The rate determining step of such an exchange process is the dissociation of the dibenzyl molecules of molecular weights 182 and 186. First order kinetics resulted with

$$k \text{ sec.}^{-1} = 10^{14.3} \exp.^{-(60 \pm 1) \times 10^3/RT}.$$

Making the assumption that the 60 k.cal./mole is the dissociation energy of the central (C-C) bond, and with the aid of thermal data it can be calculated that this is consistent with $D(C_6H_5CH_2\text{-}H) = 84$ k.cal./mole. Davidson had to make a slight correction for a small percentage decomposition which occurred, and he found that, at higher pressures, the rate of decomposition increased when compared with the rate of $C_6H_5CH_2CD_2C_6H_5$ formation. This is in agreement with the 1.5 order of the decomposition reaction as compared with the first order kinetics for the dissociation.

This work was done in a static system over the temperature range 452 - 464°C, and it is an interesting confirmation of work by Alexander[12] on the reaction between iodine and toluene in the gas phase. In the process of analysing this system, Alexander studied the decomposition of dibenzyl in the presence of hydrogen iodide, the rate of which depended on the dibenzyl concentration, and which he deduced was determined by its rate of dissociation followed by capture of the benzyl radical by hydrogen iodide. His studies were in a flow system, with

contact times of the order 0.25 second, and gave

$$k \text{ sec.}^{-1} = 10^{15.4} \exp.^{-61000/RT}.$$

Bromination of Toluene by Anderson, Scherage and VanArtsdalen.

A different kinetic method for finding the bond dissociation energy in toluene has been applied by VanArtsdalen and collaborators[6]. The method was the same as that applied by VanArtsdalen and Kistiakowsky[25] to determine the dissociation energy of the (C-H) bond in methane, and both researches depend a great deal on the classical investigations by Bodenstein[26,27] on the combination of hydrogen and bromine.

In essentials the method makes use of the fact that the heat of the gas phase reaction

$$Br + C_6H_5CH_3 \underset{k_{15}}{\overset{k_{13}}{\rightleftharpoons}} C_6H_5CH_2\cdot + HBr$$

can be expressed as

$$\Delta H = D(C_6H_5CH_2\text{-}H) - D(H\text{-}Br)$$

and that the additional relationship exists that

$$\Delta H = E_{13} - E_{15}$$

where E is the energy of activation in the appropriate direction. Since D(H-Br) is well known to be 87.7 k.cal./mole, the determination of these two activation energies would enable $D(C_6H_5CH_2\text{-}H)$ to be calculated.

The reaction between toluene and bromine can be conducted photochemically or thermally, and the former method offers the clearer evidence for the forward process in the above

reaction. This is because the temperature coefficient of the photochemical reaction is that of the rate determining step only - the forward reaction of (13). As the reaction proceeds, the concentration of hydrogen bromide builds up and inhibition occurs, but, by taking the initial rate of the process at various temperatures, the required value of E_{13} can be deduced.

In detail this procedure amounted to showing that, for conditions which were otherwise fixed, the initial rates were proportional to $(Br_2)^{\frac{1}{2}}$, which usually indicates a bromine atom reaction. The photochemical steady state concentration of these atoms would be expected to be proportional to $(Br_2)^{\frac{1}{2}}(1/\text{ Total pressure})^{\frac{1}{2}}$ since the main loss of bromine atoms is by

$$Br + Br + M = Br_2 + M \qquad (16)$$

where M is a suitable third body.

In practice they stated that the data obeyed the law

$$-d(Br_2)/dt = k(Br_2)^{\frac{1}{2}}(\text{toluene})^{\frac{1}{2}}$$

instead of

$$-d(Br_2)/dt = k(Br_2)^{\frac{1}{2}}(\text{toluene})(1/\text{Total Pressure})^{\frac{1}{2}}$$

and interpreted this as meaning that the only third body of consequence was toluene, so that for the "total pressure" the pressure of toluene should be inserted. The temperature dependence of k_{13} then gave $E_{13} = 7.2 \pm 0.6$ k.cal./mole.

It is not possible to deal with the reverse process in as simple a fashion and deduce initial rates. Instead of this, the initial rate of bromination of toluene was investigated in the presence of substantial amounts of hydrogen bromide, and a mechanism of the following type adopted:-

$$Br_2 + h\nu = 2\,Br\cdot \qquad (12)$$

$$Br\cdot + C_6H_5CH_3 = C_6H_5CH_2\cdot + HBr \qquad (13)$$

$$Br_2 + C_6H_5CH_2\cdot = C_6H_5CH_2Br + Br\cdot \qquad (14)$$

$$HBr + C_6H_5CH_2\cdot = C_6H_5CH_3 + Br\cdot \qquad (15)$$

$$Br + Br + M = Br_2 + M \qquad (16)$$

This scheme of reactions parallels those which were used by Bodenstein and by Kistiakowsky, referred to previously, and results in a rate expression for the photochemical reaction:-

$$-\frac{d(Br_2)}{dt} = \frac{k_{13}(C_6H_5CH_3)\left(\phi\, I_{abs}/k_{16}(M)\right)^{\frac{1}{2}}}{1 + k_{15}(H\,Br)/k_{14}(Br_2)}$$

Van Artsdalen et al. claimed that the toluene plus bromine data were in agreement with this form of equation, and for the purpose of finding E_{15} for (15) they found, from the hydrogen bromide inhibited experiments, values of (k_{15}/k_{14}) at three different temperatures. Thereby they deduced that $(E_{15}-E_{14}) = 5.0$ k.cal./mole. The weakest part of their arguments then follows. The reaction (14) is considered to probably have $E = 0$ approximately, but they have no direct evidence for this. It seems fairly certain that the reactions

$$H\cdot + Br_2 = HBr + Br\cdot$$

and $$CH_3\cdot + Br_2 = CH_3Br + Br\cdot$$

have low activation energies, but the case for extending this to the benzyl radical is more uncertain.

With this assumption Van Artsdalen obtains

$D(C_6H_5CH_2\text{-}H) - D(H\text{-}Br) = 7.2 - 5.0 = 2.2$ k.cal./mole,

the estimated probable error being $\pm$ 1.5 k.cal./mole, and therefore

$D(C_6H_5CH_2\text{-}H) = 2.2 + 87.7 = 89.9$ k.cal./mole.

This is the highest value observed for the dissociation energy of the side chain bond in toluene, but would be lowered slightly if the assumption noted above was incorrect. The experimental methods and findings are given in satisfying detail, and it is a difficult investigation to refute. However, Benson and Buss[28] have, in a recent paper, questioned whether reactions other than that between bromine and methane can, in fact, be held to have the same mechanism as the hydrogen plus bromine reaction and, in particular, whether under the experimental conditions used the essential equilibrium

$$Br_2 \rightleftharpoons Br + Br$$

was established and the only chain ending process was

$$Br + Br + M = Br_2 + M.$$

Chemical Equilibrium Method.

Benson and Buss[29] have studied the following equilibrium

in the gas phase at 150°C.

$$C_6H_5CH_3 + Br_2 \rightleftharpoons C_6H_5CH_2Br + HBr \quad (17)$$

Their experimental work was not extensive, only seven experiments being recorded, but they did attempt to approach the equilibrium position from both sides. They quote a value of $(7.2 \pm 0.7) \times 10^{4}$ for the equilibrium constant. Such a high result clearly implies low final concentrations of the reactants on the left hand side of the equation, and quantities of the order of 4×10^{-6} gm.moles feature in their results. From the equilibrium constant it is easy to obtain the standard free energy change of the reaction,

$$\Delta G^{\circ} = -RT \ln K_p = -9.4 \pm 0.5 \text{ k.cal./mole.}$$

For the purpose of bond dissociation energy determinations, ΔH° is a more relevant quantity, and can be obtained as $\Delta G^{\circ} + T \Delta S^{\circ}$. In order to calculate the entropy change in the reaction under investigation, Benson and Buss had to obtain a figure for the entropy of benzyl bromide - the values for the other components of the system being well-known. They estimated this quantity for benzyl bromide by standard statistical procedures, and calculated that the standard entropy change at 150°C for the reaction was equal to 3.5 ± 2 cal./mole.°C. Using this result they obtained

$$\Delta H^{\circ}_{150^{\circ}} = -8.0 \pm 0.9 \text{ k.cal./mole.}$$

This quantity can be substituted in the following

equation:-

$$\Delta H^{\circ} = D(C_6H_5CH_2\text{-}Br) + D(H\text{-}Br) - D(C_6H_5CH_2\text{-}H) - D(Br\text{-}Br)$$

and since D(H-Br) and D(Br-Br) are well-known, a value is obtained for the difference

$$D(C_6H_5CH_2\text{-}H) - D(C_6H_5CH_2\text{-}Br) = 54.7 \text{ k.cal./mole.}$$

A value for this last expression can also be derived by substitution of the experimental bond dissociation energies obtained by Szwarc, and is equal to 77.5-51 = 26.5 k.cal./mole. This discrepancy is outside the limits of error claimed for the bond energies.

Benson and Buss could not carry the argument further and decide whether Szwarc's value for $D(C_6H_5CH_2\text{-}H)$ is too low by 7.5 k.cal./mole, or whether $D(C_6H_5CH_2\text{-}Br)$ is too high by the same amount, or whether they are both in error. They were inclined to accept the first alternative, and suggested that the bond dissociation energy for toluene should be 84 k.cal./mole.

This seems to be in excellent agreement with the work on the dissociation energy of the central (C-C) bond in dibenzyl which has been mentioned earlier. It is disturbing, therefore, that the re-determination of the activation energy for the decomposition of benzyl bromide in the presence of toluene by Mearns, has led to the result 58.k.cal./mole. The data which he has obtained seem to be of greater consistency than those

of Szwarc but, using this value

$D(C_6H_5CH_2\text{-}H) - D(C_6H_5CH_2\text{-}Br) = 84 - 58 = 26$ k.cal./mole

thus returning to a bond dissociation energy difference which is not consistent with Benson and Buss' experimental work.

Electron Impact Data.

Within recent years the $C_6H_5CH_2$-H bond dissociation energy has been measured by electron impact experiments. This method consists essentially in bombarding the gaseous molecules of a substance with a beam of electrons of controlled energy. The collisions with the molecules result in fragmentation processes and, if the reaction is performed in a mass spectrometer, the nature of the reaction can be investigated by finding the mass/charge (m/e) ratio for the ions produced.

Two of the typical processes which can take place are:-

$$AB + e = AB^+ + 2e \qquad (18)$$

$$AB + e = A^+ + B + 2e \qquad (19)$$

and, by reducing the energy of the impinging electrons and following by the mass spectrometer the number of ions produced, an extrapolation procedure can lead to a value for the minimum energy necessary to cause a particular process.

In case (18) the determined value is called the ionisation potential of the molecule AB.

In case (19) the determined value is called the appearance potential of the ion A^+, and for reactions of this type:-

$$A(A^+) = D(A\text{-}B) + I(A) + (\text{Internal + Kinetic Energy of A and B}) \qquad (20)$$

$A(A^+)_{AB}$ is the appearance potential of the ion A^+ from AB. I(A) is the ionisation potential of the atom or radical A.

Although in some recent work attempts have been made to measure the kinetic energy of the ions produced, in many investigations the last terms have been assumed to be small. If this assumption has been made, or if a correction has been applied, then equation (20) offers a route to D(A-B) provided that the appearance potential of the ion A^+, and the ionisation potential of the atom or radical A are known.

There are two ways of using this relationship and the factors it contains, the so called "direct method", and the "indirect method". In the former, the ionisation potential of A is determined directly in a separate set of experiments. This is naturally rather a difficult procedure since it involves producing and injecting into the ion gun of the mass spectrometer, a reasonable concentration of the radical A. The practical difficulties in this type of experiment have led to the second method of approach, where the term I(A) is eliminated by combining the data for compound AB with similar data for compound AC.

The methods can be illustrated by examples of the data obtained for the determination of the first (C-H) bond dissociation energy in methane.

Direct Method[30].

$$CH_4 + e = CH_3^+ + H^- + 2e, \quad A(CH_3^+)_{CH_4} = 14.44 \pm 0.1 \text{ eV}.$$

$$CH_3^- + e = CH_3^+ + 2e, \quad A(CH_3^+)CH_3 = 10.00 \pm 0.1 \text{ eV}.$$

Then

$$\Delta E = D(CH_3\text{-}H) = A(CH_3^+)_{CH_4} - A(CH_3^+)_{CH_3} = \underline{4.44 \pm 0.2 \text{ eV}.}$$

Indirect Method.[31]

$$C_2H_6 + e = C_2H_5^+ + H^- + 2e,$$

$$\Delta E = A(C_2H_5^+)_{C_2H_6} = 15.20 \text{ eV}. \qquad (21)$$

$$C_3H_8 + e = C_2H_5^+ + CH_3^- + 2e,$$

$$\Delta E = A(C_2H_5^+)_{C_3H_8} = 14.50 \text{ eV}. \qquad (22)$$

Subtracting (21) from (22):-

$$C_3H_8 + H^- = C_2H_6 + CH_3^-,$$

$$\Delta E = -0.7 \text{ eV}. \qquad (23)$$

This result is then combined with the following equation which can be derived from the heats of formation of the hydrocarbons concerned and the heat of dissociation of hydrogen:-

$$C_2H_6 + CH_4 = C_3H_8 + 2H^-,$$

$$\Delta E = 5.08 \text{ eV}. \qquad (24)$$

Hence from (23) and (24):-

$$CH_4 = CH_3^- + H-$$

$$\Delta E = 4.38 \text{ eV.}$$

The main applications of these methods have been to simple aliphatic compounds, particularly the hydrocarbons and, where comparison with other data is possible, as in the example quoted, the agreement has been very good, especially in view of the difficult experimental techniques required and the nature of the results. The actual determination of an accurate appearance potential is by no means an easy matter, and while it is not the concern of this work to deal with these difficulties in detail, some of them can be outlined.

The energy of the electrons used does not lie within closely confined limits because, in addition to the energy imposed upon them by the accelerating potential, there is the normal spread of kinetic energies characteristic of the temperature at which they were formed. As a result, a graph of ion current produced against the electron accelerating voltage, tends to be curved and to cut the voltage axis obliquely. This makes the minimum energy difficult to ascertain. Usually a comparison is made between the ionisation efficiency of AB and that of an inert gas with which AB is mixed during the course of an experiment, the

ionisation potential of the inert gas being known from spectroscopic data.

In application to the bond dissociation energy in toluene both the direct and indirect methods have been used. Schissler and Stevenson[8] measured the appearance potentials of the benzyl ion from toluene and dibenzyl and derived the dissociation energy of the $C_6H_5CH_2$-H bond by the indirect method as follows:-

$$\left.\begin{aligned} C_6H_5CH_3 &= C_7H_7^+ + H^- + e, \\ A(C_7H_7^+)_{(25)} &= D(C_6H_5CH_2\text{-}H) + I(C_6H_5CH_2\cdot) \end{aligned}\right\} \quad (25)$$

$$\left.\begin{aligned} (C_6H_5CH_2)_2 &= C_7H_7^+ + C_6H_5CH_2^- + e, \\ A(C_7H_7^+)_{(26)} &= D(C_6H_5CH_2\text{-}CH_2C_6H_5) + I(C_6H_5CH_2\cdot) \end{aligned}\right\} \quad (26)$$

Subtracting equation (25) from equation (26) we obtain:-

$$\left.\begin{aligned} (C_6H_5CH_2)_2 + H^- &= C_6H_5CH_3 + C_6H_5CH_2^-, \\ \Delta H_{(27)} &= D(C_6H_5CH_2\text{-}CH_2C_6H_5) - D(C_6H_5CH_2\text{-}H) \\ &= A_{(26)} - A_{(25)} \end{aligned}\right\} \quad (27)$$

Equation (27) is then subtracted from the following equation for which the heat of reaction was calculated from known thermochemical data:-

$$\left.\begin{aligned} (C_6H_5CH_2)_2 + 2H^- &= 2\ C_6H_5CH_3, \\ \Delta H_{(28)} &= -4.66\ eV \end{aligned}\right\} \quad (28)$$

Hence $C_6H_5CH_2\text{-}H = C_6H_5CH_2^- + H^-$,

$$\Delta H = D(C_6H_5CH_2\text{-}H) = 4.66 + A_{(26)} - A_{(25)} \qquad (29)$$

The experimental values for the appearance potentials $A_{(25)}$ and $A_{(26)}$ were 11.85 ± 0.1 eV and 10.53 ± 0.1 eV, and the value for the appearance potential of $C_7H_7^+$ from toluene was checked by thermochemical calculations using a measured value for the appearance potential of $C_7H_7^+$ from ethylbenzene. Substitution of these values in equation (29) leads to $D(C_6H_5CH_2\text{-}H)$ = 77 ± 3 k.cal./mole in agreement with the value found by Szwarc.

This work was followed by a paper by Lossing et al.[9] who used the direct method for the determination of the dissociation energy. They measured the ionisation potential of the benzyl ion, the supply of benzyl radicals being obtained from the pyrolysis of benzyl iodide. The value observed was 7.73 ± 0.08 eV and together with the value for the appearance potential of the benzyl ion from toluene, this leads to $D(C_6H_5CH_2\text{-}H)$ = 94.8 k.cal./mole.

Recent studies on the appearance and ionisation potentials in the St.Andrews laboratories by Hamer[32] confirm this high value for the dissociation energy when derived from the direct method. His value for the appearance potential of the benzyl ion from toluene is 12.34 ± 0.12 eV, and for the ionisation potential of the benzyl radical 8.05 eV and

hence the bond dissociation energy

$$D(C_6H_5CH_2\text{-}H) = 4.29 \text{ eV} = 99 \text{ k.cal./mole.}$$

Clearly in view of the chemical evidence for the easy extraction of a hydrogen atom from toluene, these values seem unreasonably high.

A criticism of the work published by Schissler and Stevenson was made by Lossing et al.[10] on the grounds that the ionisation potential of the benzyl radical, calculated using the known thermochemical data required in the following relations, together with the appearance potentials measured by Schissler and Stevenson, is higher than the directly measured value by approximately 0.7 eV.

$$\left.\begin{aligned} C_6H_5CH_3 &= C_6H_5CH_2^+ + H\text{-} + e, \\ A(C_6H_5CH_2^+)_{(30)} &= D(C_6H_5CH_2\text{-}H) + I(C_6H_5CH_2\text{-}) \end{aligned}\right\} (30)$$

$$\left.\begin{aligned} (C_6H_5CH_2)_2 &= C_6H_5CH_2^+ + C_6H_5CH_2\text{-} + e, \\ A(C_6H_5CH_2^+)_{(31)} &= D(C_6H_5CH_2\text{-}CH_2C_6H_5) + I(C_6H_5CH_2\text{-}) \end{aligned}\right\} (31)$$

$$\left.\begin{aligned} C_6H_5CH_3 &= C_6H_5CH_2\text{-} + H, \\ \Delta H_{(32)} &= D(C_6H_5CH_2\text{-}H) \\ &= \Delta H_f(H) + \Delta H_f(C_6H_5CH_2\text{-}) - \Delta H_f(C_6H_5CH_3) \end{aligned}\right\} (32)$$

$$\left.\begin{aligned} (C_6H_5CH_2)_2 &= 2\ C_6H_5CH_2\text{-}, \\ \Delta H_{(33)} &= D(C_6H_5CH_2\text{-}CH_2C_6H_5) \\ &= 2\ \Delta H_f(C_6H_5CH_2\text{-}) - \Delta H_f(C_6H_5CH_2)_2 \end{aligned}\right\} (33)$$

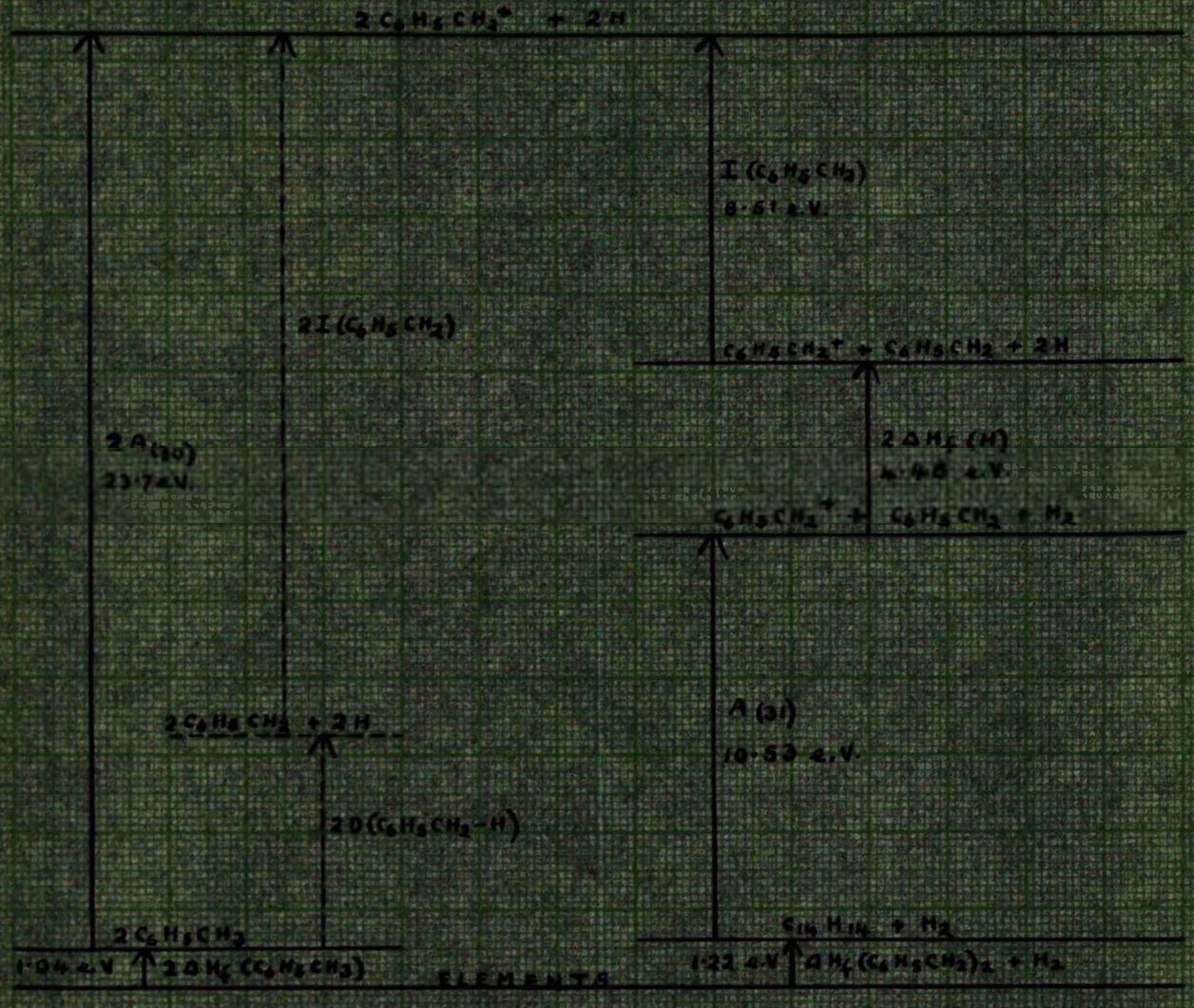

2 C6H5CH2+ + 2H
I (C6H5CH2)
8·61 e.V.
2I (C6H5CH2)
C6H5CH2+ + C6H5CH2 + 2H
2 A (30)
23·7 e.V.
2 ΔHf (H)
4·46 e.V.
C6H5CH2+ + C6H5CH2 + H2
2 C6H5CH2 + 2H
A (31)
10·53 e.V.
2D (C6H5CH2-H)
C14H14 + H2
2 C6H5CH2
1·04 e.V.
2 ΔHf (C6H5CH3)
ELEMENTS
1·22 e.V.
ΔHf (C6H5CH2)2 + H2

FIGURE (1).

Eliminating $D(C_6H_5CH_2\text{-}H)$ and $D(C_6H_5CH_2\text{-}CH_2C_6H_5)$ from equations (30) and (31) by substitution from equations (32) and (33):-

$$A_{(30)} = \Delta H_f(H) + \Delta H_f(C_6H_5CH_2\text{-}) - \Delta H_f(C_6H_5CH_3) + I(C_6H_5CH_2\text{-}) \quad (34)$$

$$A_{(31)} = 2\ \Delta H_f(C_6H_5CH_2\text{-}) - \Delta H_f(C_6H_5CH_2)_2 + I(C_6H_5CH_2\text{-}) \quad (35)$$

Subtracting (35) from twice (34):-

$$I(C_6H_5CH_2\text{-}) = 2\ A_{(30)} - A_{(31)} + 2\ \Delta H_f(C_6H_5CH_3) - 2\ \Delta H_f(H) - \Delta H_f(C_6H_5CH_2)_2$$

The calculation is also shown diagramatically in Fig.(1).

It was suggested that the discrepancy could be partly explained by an error in the appearance potentials caused by the large curvature at the foot of the ionisation efficiency curves, and also by the presence of excess energy terms not eliminated during the calculation.

Further experiments using deuterated toluene $C_6H_5CD_3$ were made by Lossing et al. to determine the appearance potential for the benzyl ion. It was found that on electron bombardment both hydrogen and deuterium atoms were lost from the compound showing the occurrence of the two processes (36) and (37):-

$$C_6H_5CD_3 + e = C_6H_5CD_2^+ + D + 2\,e \qquad (36)$$

$$C_6H_5CD_3 + e = C_6H_4CD_3^+ + H^- + 2\,e \qquad (37)$$

Lossing et al. viewed this as the formation of benzyl and tolyl ions and noted that their relative proportions were in a ratio to be expected if all the "hydrogens" were equivalent in the dissociation. For the purpose of evaluating $D(C_6H_5CH_2\text{-}H)$ it is necessary that the measured energy is that required exclusively for reaction (36), and, although it was expected that I(tolyl)> I(benzyl) and that therefore reaction (36) should predominate, the process of formation of a benzyl ion from toluene did not appear to be as straightforward as would be expected.

By a series of skilful deductions using the mass spectra of o, m, and p-deuterotoluene, toluene-α-d_1, -α-d_2 and ethylbenzene - α - β d_5, Rylander, Meyerson and Grubb[33] were able to show that all the hydrogen atoms are equivalent for the purpose of making a $C_7H_7^+$ ion from toluene, and they suggested that this could only be the case if the ion formed was the tropylium ion. There is not, however, the same precise evidence for stating that electron bombardment of a benzyl radical leads to the formation of a tropylium ion.

Since Rylander et al. conclude that in forming $C_7H_7^+$ from toluene there is a loss of identity of the hydrogen atoms of the latter, they picture the process as occurring:-

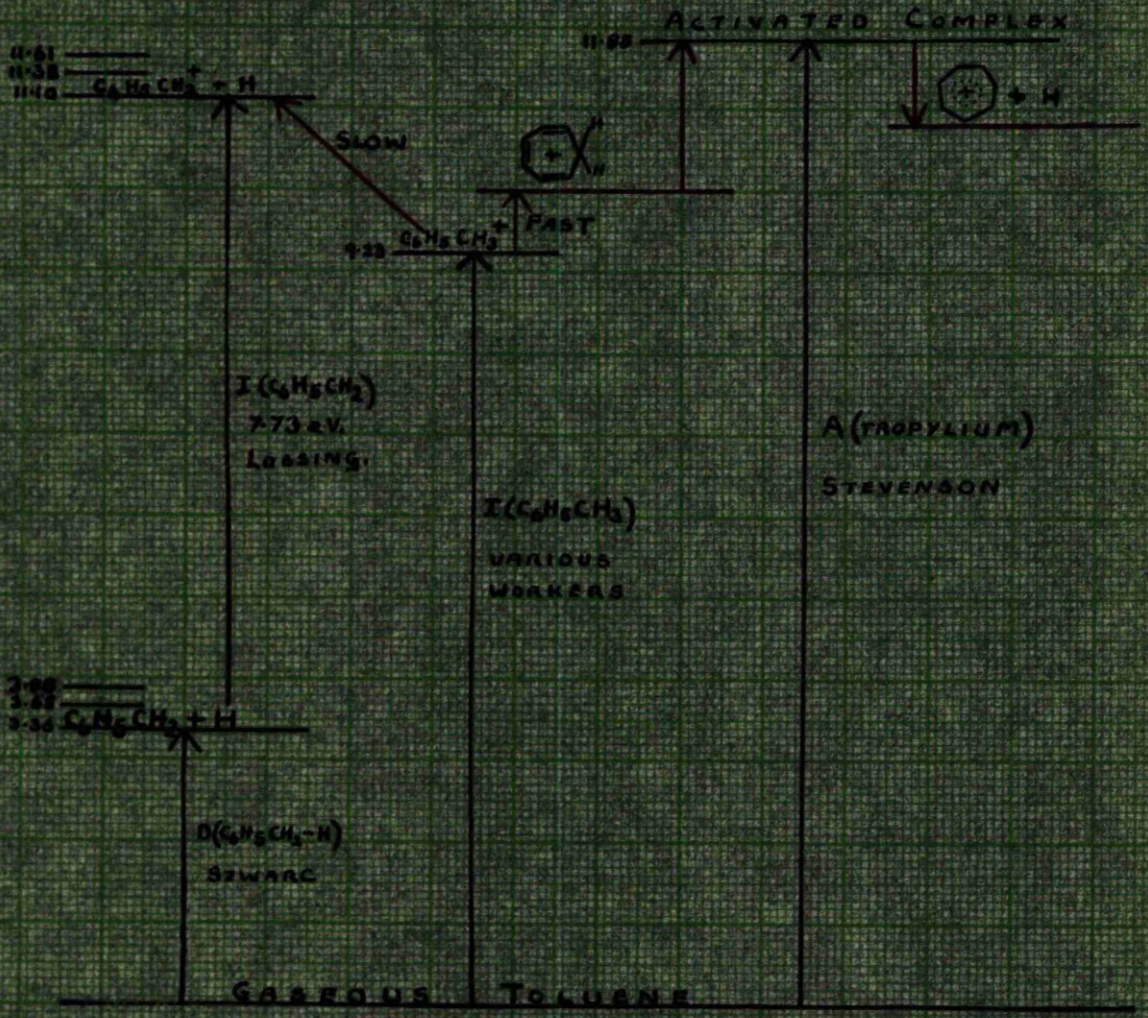
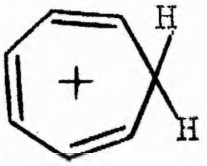

ACTIVATED COMPLEX
11·61
11·38
11·18
SLOW
FAST
9·22
I(C6H5CH2)
7·73 e.V.
Lossing.
I(C6H5CH3)
VARIOUS
WORKERS
A(TROPYLIUM)
STEVENSON
2·48
3·87
3·34
D(C6H5CH2-H)
SZWARC
GASEOUS
TOLUENE

FIGURE (2).

toluene + e =  + 2 e

giving the cycloheptatriene molecule ion. This ion then passes via an activated complex to the tropylium ion plus a hydrogen atom:-

 =  + H-

and cannot give a benzyl ion. They consider that in the equation:-

$$D(C_6H_5CH_2\text{-}H) = A(C_7H_7^+)_{toluene} - I(C_7H_7)$$

the experimental appearance potential of 11.8 eV refers to the formation of the tropylium ion, while $I(C_7H_7)$ is the energy absorbed in the process:-

$$C_6H_5CH_2^- = C_6H_5CH_2^+ + e.$$

Thus the use of this equation is invalid for the purpose of measuring the bond dissociation energy in toluene. The relationships between the various energies they consider are shown in the diagram Fig.(2). It must be noted that they suggest that the tropylium ion is at a lower energy level than the benzyl ion, and that they assume $D(C_6H_5CH_2\text{-}H)$ to be 77.5 k.cal./mole. If the higher values of 84 and 89 k.cal./mole are used, it can be seen that the sum of

$D(C_6H_5CH_2\text{-}H)$ + $I(C_6H_5CH_2\text{-})$ approaches more closely to 11.8 eV - the appearance potential of the tropylium ion. For $D(C_6H_5CH_2\text{-}H)$ = 84 k.cal./mole (3.65 eV) the addition of Lossing's ionisation potential for the benzyl radical of 7.73 eV gives 11.38 eV, and while this is still 0.47 eV below the appearance potential of the tropylium ion, it is of interest to note that Hamer, when repeating the determination of the ionisation potential of the benzyl radical, found 8.03 eV. If this is used, the discrepancy between the energy levels of the ionised radical and the appearance potential of the tropylium ion effectively disappears. In this case, the part of the diagram in red could be removed and the activated complex of Rylander et al. taken to be the level of the benzyl and tropylium ions.

The introduction of this tropylium ion conception into the field of discussion certainly complicates the position, but it seems to the author that a more serious difficulty appears to be the discrepancies between the values given by different workers for the same process. Each of these workers may have tested their apparatus by comparing their ionisation potential values for substances such as the inert gases, acetylene, etc., with spectroscopic values and found agreement to about 0.1 eV or less, but the same workers differ markedly on some of the appearance potentials of interest

to this thesis. Thus Hamer in St.Andrews found:-

$A(C_6H_5CH_2^+)_{\text{benzyl chloride}} = 10.77 \pm 0.15$ eV,

but he quotes values of 11.13 ± 0.1 eV due to Franklin and Lumpkin[34], and 10.35 ± 0.1 eV due to Lossing et al.[35] Since discrepancies of 0.25 eV amount to approximately 6 k.cal./mole, the discriminatory power of electron impact data in this particular discussion is rather poor.

A comparison of the relative merits of the values 77.5, 84 and 89.5 k.cal./mole for $D(C_6H_5CH_2\text{-}H)$ will not be made at this stage.

The experimental work of this thesis attempts to produce further evidence on the pyrolysis of toluene, and the discussion given later considers the additional facts together with the data summarised above.

THE PRESENT INVESTIGATION.

The only published kinetic results on the pyrolysis of toluene which were available when the following experiments began were those due to Szwarc. The description and discussion of his data given earlier show the points on which it was felt that further information was desirable.

In the first place, the reactions postulated by Szwarc to explain the formation of methane:-

$$H\cdot + C_6H_5CH_3 = C_6H_6 + CH_3\cdot \qquad (1)$$

$$CH_3\cdot + C_6H_5CH_3 = CH_4 + C_6H_5CH_2\cdot \qquad (2)$$

seemed to require justification. It is possible to argue that:-

$$C_6H_5CH_3 = C_6H_5\cdot + CH_3\cdot \qquad (3)$$

followed by:-

$$C_6H_5\cdot + C_6H_5CH_3 = C_6H_5{-}H + C_6H_5CH_2\cdot \qquad (4)$$

and

$$CH_3\cdot + C_6H_5CH_3 = CH_3{-}H + C_6H_5CH_2\cdot \qquad (5)$$

could be equally effective in explaining the products. The crucial point is, of course, to check the existence of reaction (1), and this involves the generation of hydrogen atoms in the presence of toluene, preferably at or near pyrolysis temperatures.

There have been many investigations of the reactions of hydrogen atoms using photosensitisation or discharge tube methods to produce the atoms. However, such work has not

been done at high temperatures, and after consideration of the need to simulate pyrolysis conditions as closely as possible, it was decided to use an alternative method of test. When investigating suspected chain decompositions resort has often been made to the addition of thermally unstable substances which produce a desired species of radical, for example, when mercury dimethyl was added to butane[36,37] which was undergoing thermal decomposition. This technique has not been applied to investigations of hydrogen atom reactions, two possible reasons for this being that it is desirable that a source of hydrogen atoms shall be used, say XH, where dissociation is sufficiently rapid, and where the radical X will not interfere with the process being studied.

An investigation by McCrae[38] in St.Andrews had shown that fluorene decomposed at a rate given by:-

$$k_{(sec^{-1})} = 10^{12.9} \exp.^{-68500/RT}$$

forming hydrogen and difluorenyl, and thus seemed to be a suitable additive for the toluene pyrolysis. The rate of decomposition is faster than that of toluene, and can provide hydrogen atoms at temperatures where the toluene decomposition is small but definite, and the fluorenyl radical is more stable than the benzyl radical. The projected experiment was, therefore, to pyrolyse fluorene in admixture with excess

toluene. If evidence for reaction (1) was obtained, it was thought that by using deuterium as a carrier gas, a comparison could be made between the rate of (1) and that of:-

$$H\text{-} + D_2 = HD + D\text{-} \qquad (6)$$

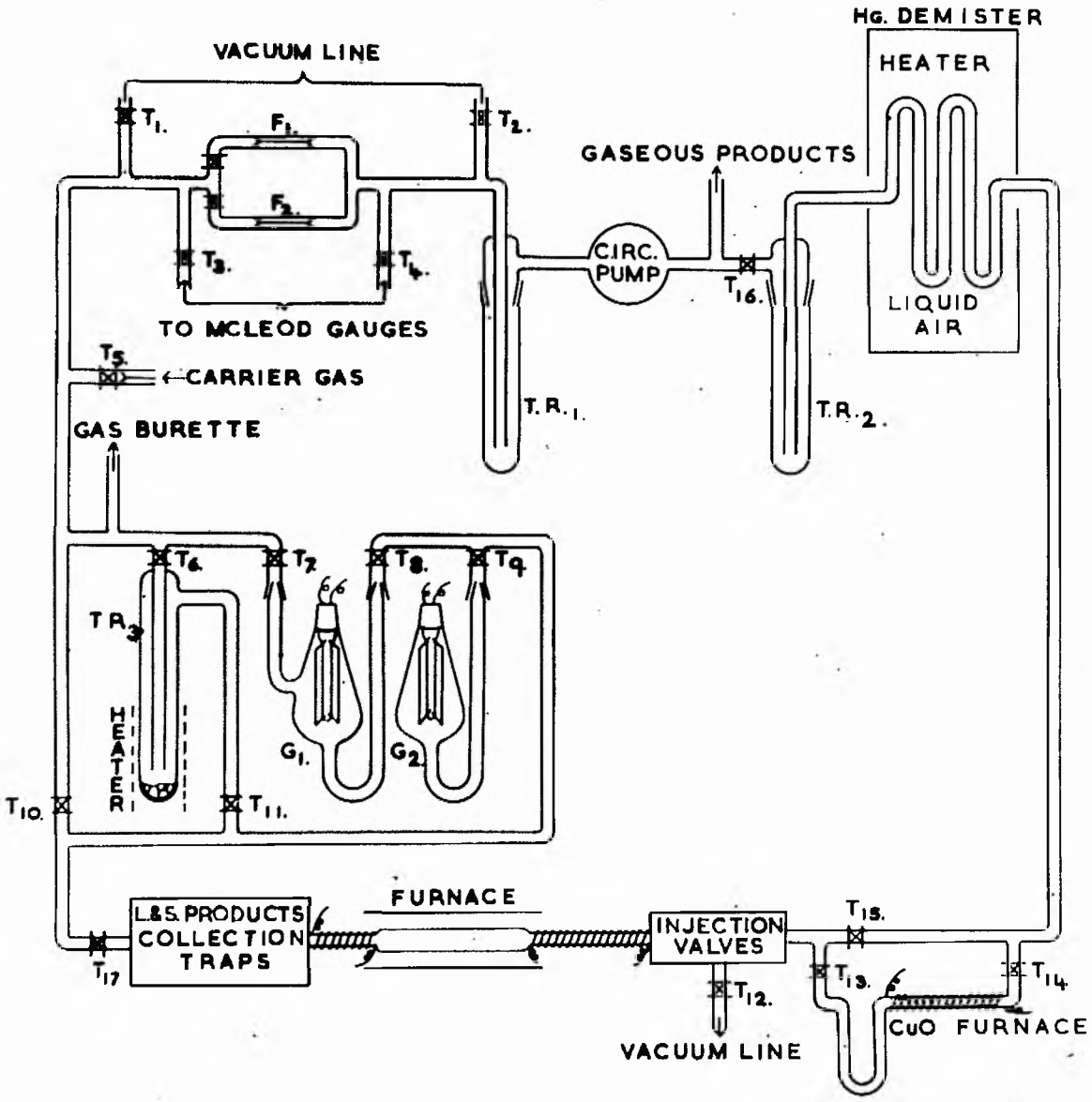
Since the activation energy of (6) is known, some evidence concerning (1) might result.

The literature summary given earlier indicates the other weak points in Szwarc's data. There was not sufficient proof of first order kinetics using independent variations of concentration and contact time, and the evidence on the nature of the products was inadequate.

In designing apparatus to permit a more critical evaluation of the pyrolysis, it was decided to use a flow system with a circulating carrier gas, and to inject the reactants into this gas. This permits the time of contact to be controlled, essentially by the carrier gas flow rate, and the amounts of injected materials to be varied. This technique differs from that used by Szwarc, who used a stream of toluene vapour through his reaction vessel and had no other carrier gas. In these latter conditions, a change in flow rate of toluene was brought about by altering the driving pressure of this material. Such an alteration of pressure gave, of course, an alteration in concentration

in the reaction chamber. The superiority of the independent carrier gas technique for this purpose is offset by one limitation; the mercury vapour pumps used to produce the carrier gas circulation cannot operate at high gas pressures, and since the reactant pressure has to be lower than that of the carrier gas, it was not convenient to exceed reactant pressures of about 2mm.

Since it was desired to use the same range of temperature for the investigation as Szwarc, and to use small percentages of decomposition, the analytical techniques had to be capable of dealing with even smaller amounts of materials than were available to Szwarc. Some of the products are solids, and the only options for their analysis in quantities of up to 4mgm. seemed to be mass spectrometry or gas chromatography. As far as the involatile compounds were concerned, the methods and apparatus for both would need to be produced as detailed information for such compounds was not available. It was decided to adapt and improve the solids handling technique, using the existing mass spectrometer, rather than undertake gas chromatographic work on some very involatile materials.



FLOW SYSTEM

FIGURE (3).

APPARATUS.

General Description.

The apparatus shown diagramatically in Fig.(5) was a low pressure flow system of the type commonly used in kinetic studies. Continuous circulation of a carrier gas was maintained by a mercury vapour pump, and the gas was freed from mercury vapour by passage through the demister and traps $T.R._1$ and $T.R._2$, which were surrounded by liquid air baths.

The reactants were introduced into the gas stream through the injection valves before it passed into the silica reaction vessel in the furnace. Collecting traps in series Fig.(7) for solid and liquid products were arranged after the furnace, and this combination was repeated in parallel and in triplicate to permit three runs to be achieved before opening the equipment. The gas stream, freed from condensible materials, passed through the thermal conductivity gauge G_1, which was used to follow the change in hydrogen content, and then returned to the pump via a capillary F_1 or F_2. The pressure drop across the capillary was measured using a double McLeod gauge, and used to calculate the flow rate.

It was found convenient to include two by-passes to

the main circulation route, which could be brought into action by appropriate operation of taps. The first allowed the gas to flow through the heated sodium trap $T.R._3$, thereby ensuring removal of oxygen; this by-pass was closed before actual decomposition runs commenced. The other by-pass section contained a heated copper oxide furnace which could be brought into circuit in the interval between runs in order to remove accummulating hydrogen in the circulating gas.

The flow system was connected in three places, taps T_1, T_2 and T_{12} to a vacuum line, and was evacuated by an Edwards Speedivac rotary oil pump and a single stage mercury diffusion pump. Together, these were capable of lowering the pressure in the apparatus to 10^{-5} mm.Hg. The carrier gas storage and injection system, and the collection system for the gaseous products were also connected to the flow system and vacuum line. All glass lines from the injection valves to the collection traps for solids were wound with Nichrome tape and heated electrically to prevent involatile reactants or products from condensing out.

Description of Apparatus in Detail.

Carrier Gas Storage and Injection System.

After purification the carrier gases were stored in

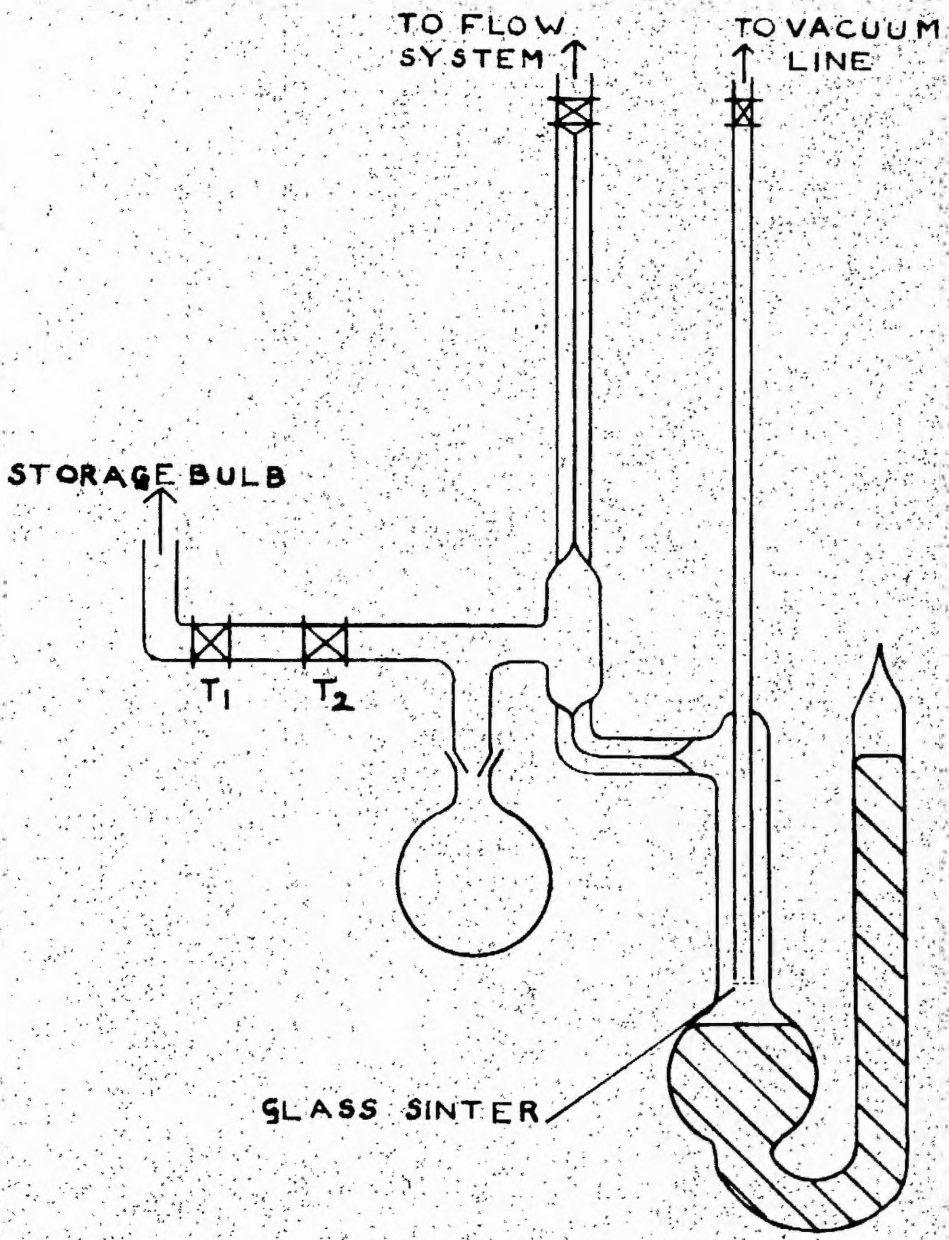

TO FLOW SYSTEM
TO VACUUM LINE
STORAGE BULB
T1
T2
GLASS SINTER

FIGURE (4).

5 litre bulbs which were attached by a greased ground joint to a manostat; this allowed a constant pressure of gas to be injected into the flow system, and was constructed as in Fig.(4). The volume of the manostat was adjusted so that one filling gave a pressure of approximately 3 mm. gas in the flow system.

Circulation of Carrier Gas and Measurement of Rate of Flow.

The rate of flow of the carrier gas was calculated from the pressure drop across a calibrated capillary F_1 or F_2, the pressure readings being taken on a double McLeod gauge.

From Meyer's formula:-

$$V_o = \frac{\pi r^4}{16 \eta L} \frac{(P^2 - P_o^2)}{P_o}$$

where V_o = Volume of gas emerging from the capillary.

P = Pressure of gas entering the capillary.

P_o = Pressure of gas emerging from the capillary.

η = Coefficient of viscosity of the gas.

L = Length of the capillary.

r = Radius of the capillary.

Since the number of moles of gas = $P_o V_o / RT$.

Rate of flow of gas in moles per second

$$= \frac{\pi r^4}{16 \eta L} \frac{(P^2 - P_o^2)}{RT}$$

TABLE II

Capillary	Length in cm.	Constants for Calculation of Rate of Flow of Carrier Gas $\times 10^6$		
		N_2	H_2	He
1	5.00	1.058	2.155	0.955
2	12.55	0.422	0.832	0.380

Radius of capillaries = 0.08979 cm.

Therefore rate of flow = $K(P^2 - P_o^2)$ moles per second

where $K = r^4\pi / 16\eta LRT$ = capillary constant.

A piece of uniform capillary tubing was obtained and its radius determined by introducing a thread of mercury into the tube, measuring its length accurately, and then weighing the thread. Two pieces of this tube, one 5 cm. and the other 12.55 cm. long, were sealed into the flow system with a tap at one end of each, so that either could be used to regulate the rate of flow of the carrier gas. The constants were calculated for each capillary for nitrogen, hydrogen and helium, and used in conjunction with the McLeod readings for P and P_o to determine the rate of flow, see Table (II). It had been found previously that the rate of flow calculated in this way differed from the value obtained by a direct calibration, so in order to determine the correct rate of flow, a known volume of dry air was passed through each capillary in a known time; the pressure difference on the McLeods being read at the same time. A calibration graph was drawn for each capillary with the true and calculated rates of flow as variables, Fig.(5), and this was used in all calculations of the time of contact to convert the calculated rate of flow obtained from the McLeod readings and capillary constant to the true rate of flow.

The carrier gas was pumped round the flow system by a

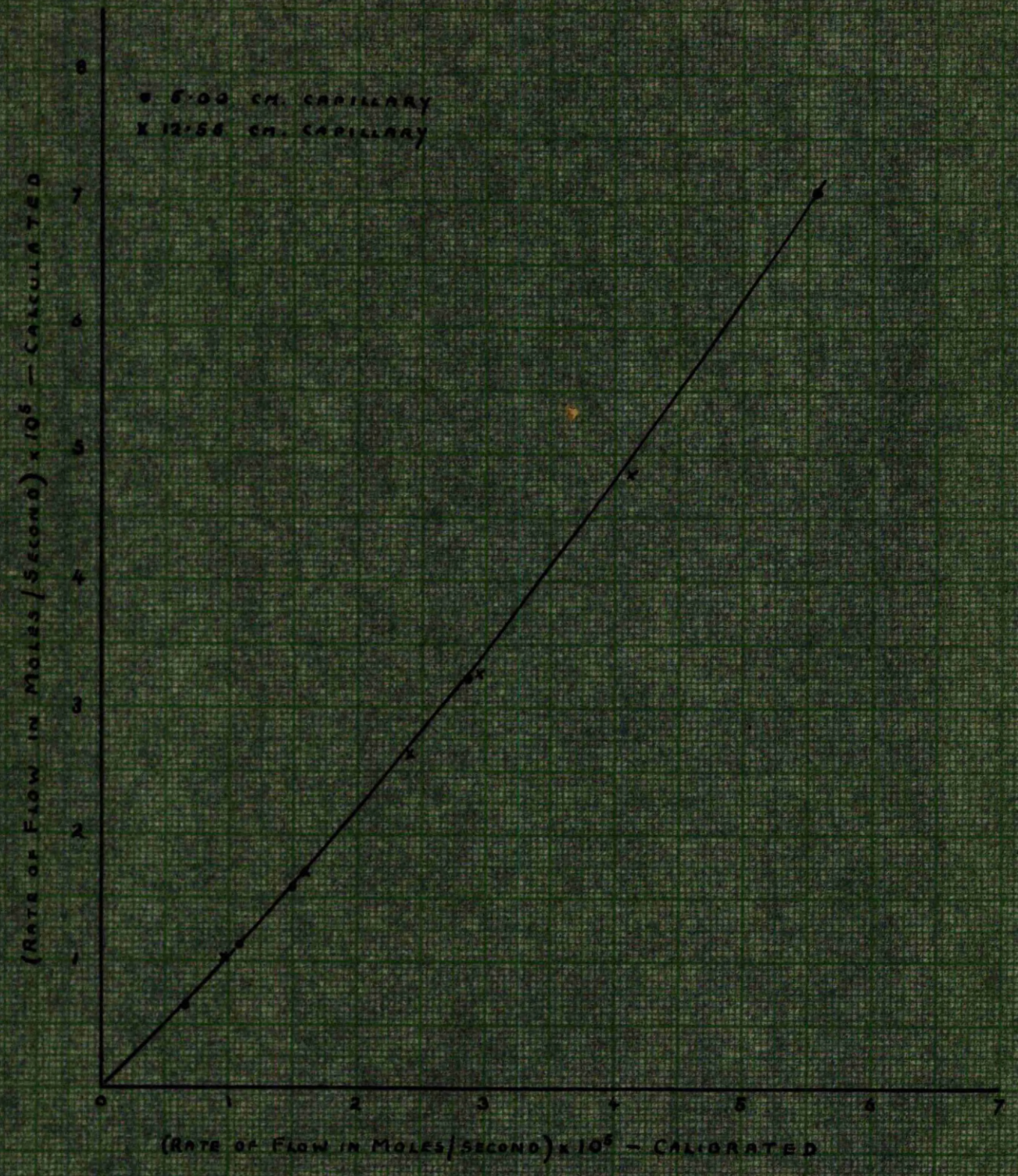

• 6·00 cm. capillary
X 12·56 cm. capillary
(Rate of Flow in Moles/Second) x 10⁵ — Calculated
(Rate of Flow in Moles/Second) x 10⁵ — Calibrated
0
1
2
3
4
5
6
7
8

FIGURE (5).

mercury vapour pump. The boiler of the pump was surrounded by a Wood's metal bath, the temperature of which was controlled by a Sunvic energy regulator - type T.Y.B. The optimum temperature for this bath was found by injecting the required pressure of carrier gas into the flow system, measuring the pressure drop across the capillary and calculating the difference $(P^2 - P_o^2)$ for various bath temperatures. The results were expressed graphically as shown in Fig.(6). For experimental work the bath temperature corresponding to the flattest part of the curve was used. The stem of the pump was wound with Nichrome tape and heated to about 200°C, as it was found that the temperature of the stem had a large effect on the speed of the pump and the constancy of the rate of flow of the carrier gas.

Calculation of the Time of Contact.

The time of contact of the reactants with the hot zone of the reaction vessel was calculated using the formula:-

$$t_{(\text{second})} = V \times P \times 273/\text{Rate of flow} \times 22400 \times 760 \times T^{\circ}K$$

where V = Volume of reaction vessel.

P = Pressure in reaction vessel.

T = Temperature of reaction vessel.

and the rate of flow is expressed in moles per second.

Two comments may be made on quantities in this formula:-

(a) The pressure (P) is the sum of the partial pressures of

TABLE III

Cathetometer Readings.	McLeod Readings.
4.00	4.05
7.42	7.40
7.30	7.34
7.37	7.40
7.39	7.42
3.71	3.77
3.74	3.80
3.98	3.90

all the gases in the reaction vessel, and its value was taken to be the same as the reading on the high pressure side of the double McLeod gauge. To check that this procedure was valid, a direct determination of (P) was made by glass-blowing a wide mercury manometer on to the exit tube of the reaction vessel immediately below the silica-pyrex seal. The pressure recorded by this manometer was read using a cathetometer, and the values obtained compared with the McLeod readings, see Table (III).

(b) The rate of flow in moles per second is equal to the sum of the rates of flow of all the gases present.

If the rate of flow of nitrogen = y moles/sec.

and the rate of flow of all other vapours present = x moles/sec.

Pressure in the reaction vessel = P mm.

The partial pressure of nitrogen in the reaction vessel is:-

$$P_{N_2} = P.(y/x + y)$$

The partial pressure of the other gases present is:-

$$P\ (x/x + y)$$

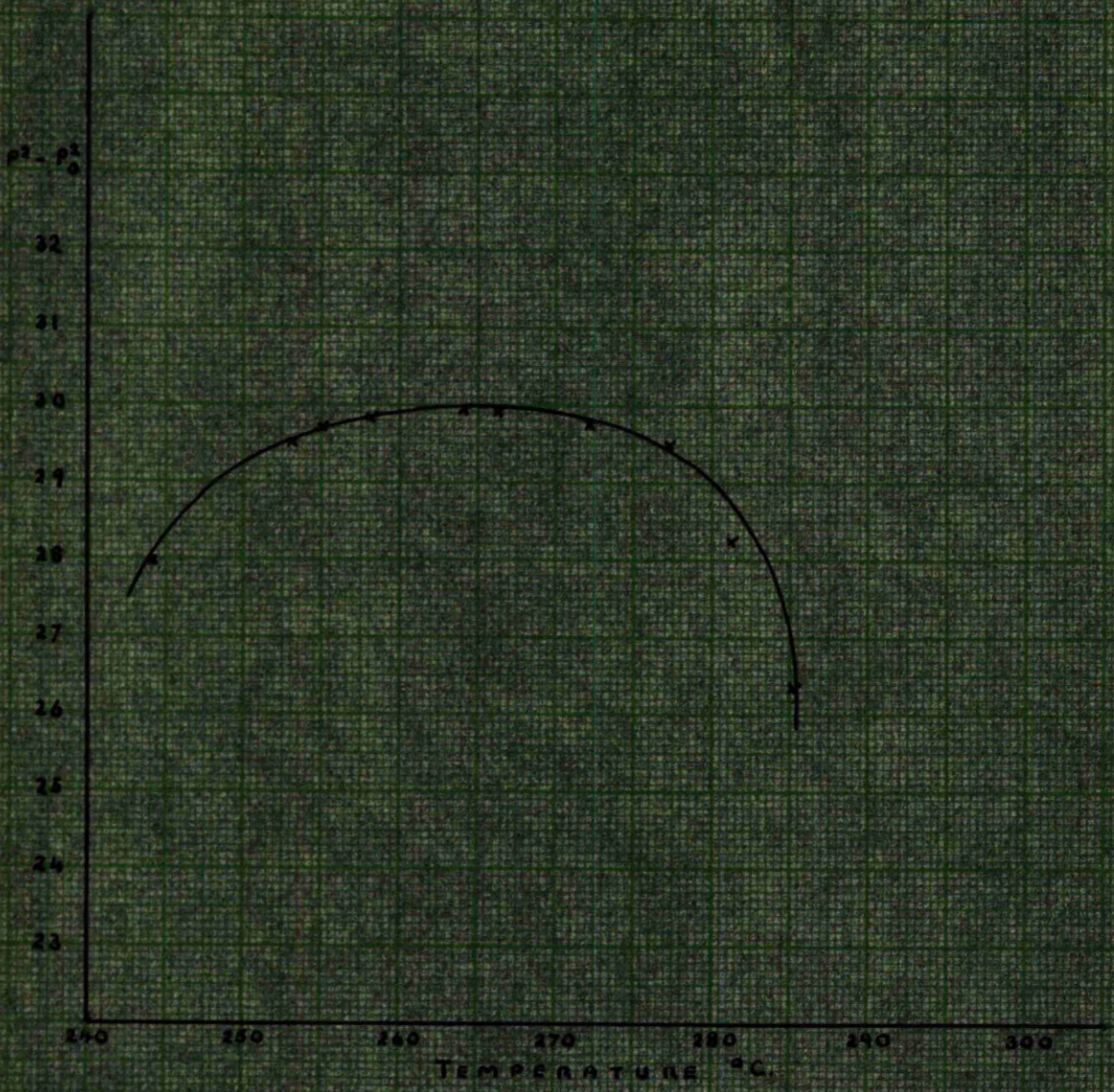

$\rho^2 - \rho_0^2$
32
31
30
29
28
27
26
25
24
23
240
250
260
270
280
290
300
TEMPERATURE °C.

FIGURE (6).

Time of contact = Reactor volume / Rate of flow in moles per second at the temperature and pressure in the reactor.

$$= \frac{\text{Reactor volume}}{y \cdot 22400 \cdot \frac{760}{P_{N_2}} \cdot \frac{T}{273}}$$

$$= \frac{\text{Reactor volume} \cdot 273 \cdot P}{(x + y) \cdot 22400 \cdot 760 \cdot T}$$

Therefore, in calculating the time of contact, the rate of flow of reactants must be added to the rate of flow of the carrier gas to give the total rate of flow.

Sodium Trap.

The sodium trap on the main apparatus (trap T.R.$_5$ Fig.(3)) was used for further purification of the nitrogen carrier gas if it was suspected that this contained oxygen.

A nickel crucible was filled with pieces of dry sodium which had been kept under vacuum, and not material which had been stored under toluene, and the trap was evacuated for some time as soon as it had been filled. The heater for the trap was made from an iron tube covered with asbestos paper, then wound with Nichrome tape and finally covered with several layers of asbestos paper. The trap was heated to 500°C.

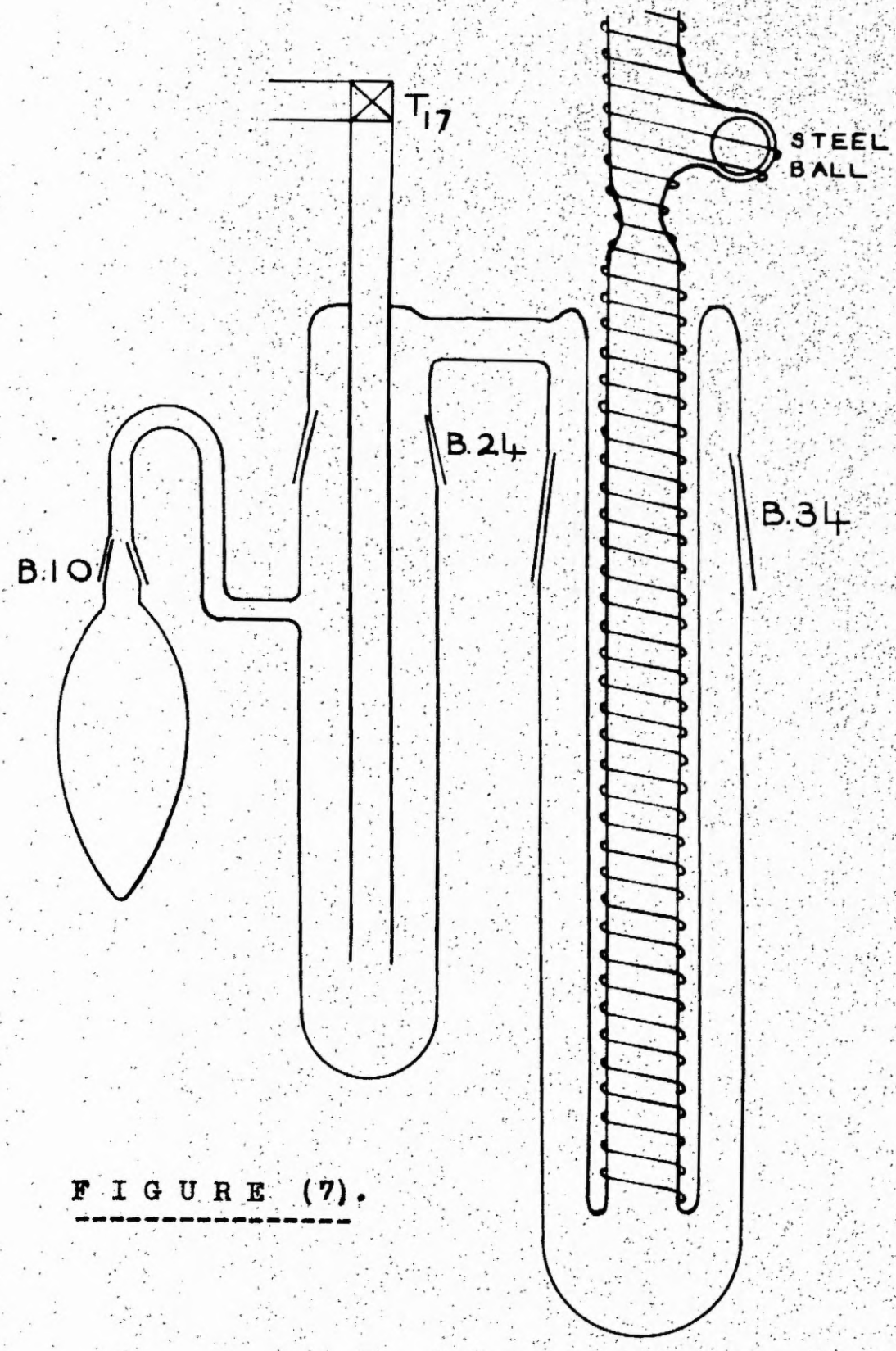


FIGURE (7).

Collection Systems.

(1) Solid Products.

In the first experiments using fluorene, the solid products were collected in three U-tubes joined in series. During the first run a cold bath was placed round the third U-tube, and at the end of the run, the other two were warmed to drive the solid into the cooled tube. This system did not give very consistent results for the amounts of fluorene collected, so the U-tubes were replaced by three traps in parallel, where the central tube was heated to drive the products into the removable portion - see Fig.(7). These were isolated from the flow system on the reaction vessel side by lowering half-inch stainless steel balls on to ground seats on the tops of the traps. The balls could be raised by a magnet and placed in a pocket at the side of the flow line. On the far side of the reaction vessel, the traps were isolated by three taps.

In later experiments when toluene was used, a smaller trap with B.24 ground glass joints, on the side of which was a small pear shaped trap with B.10 joints, was attached to each heated trap.

During a run, the liquid and solid products were frozen out in the heated traps, which were surrounded by baths at -183°C. At the end of a series of runs, the apparatus was

TABLE IV

Bulb Volume	Ratio of Total Volume to Bulb Volume.
143.6	1.48
143.8	1.49
155.0	1.43
108.0	1.60
144.0	1.46

evacuated, the ball valves and taps closed, thus sealing off the collecting system from the rest of the apparatus, and the liquid distilled, first into the B.24 and then into the B.10 traps which were surrounded by liquid air baths, a bath at $-20^{o}C$ being kept round each heated trap. The B.10 traps were then withdrawn and sealed with ground glass stoppers.

(2) Gaseous Products.

At the end of a run, the tap (T_{16} Fig.(3)) on the low pressure side of the circulation pump was closed, and the gaseous products and carrier gas passed through a two-way tap (T_{17} Fig.(8)) into a Toepler pump. The Toepler pump was then used to force the gases through the other side of the two-way tap into the apparatus shown in Fig.(8), which consisted of a manometer to which was attached a bulb of known volume by means of a ground glass joint.

The volume of the whole of this piece of the apparatus above the two-way tap, was found by expanding a known volume of gas at atmospheric pressure into the apparatus and measuring the final pressure on the manometer. When the gases were required for analysis in the mass spectrometer, the bulb was removed and, since the ratio of the bulb volume to the volume of the whole of this piece of the apparatus was known, the total volume of gas present could be calculated,

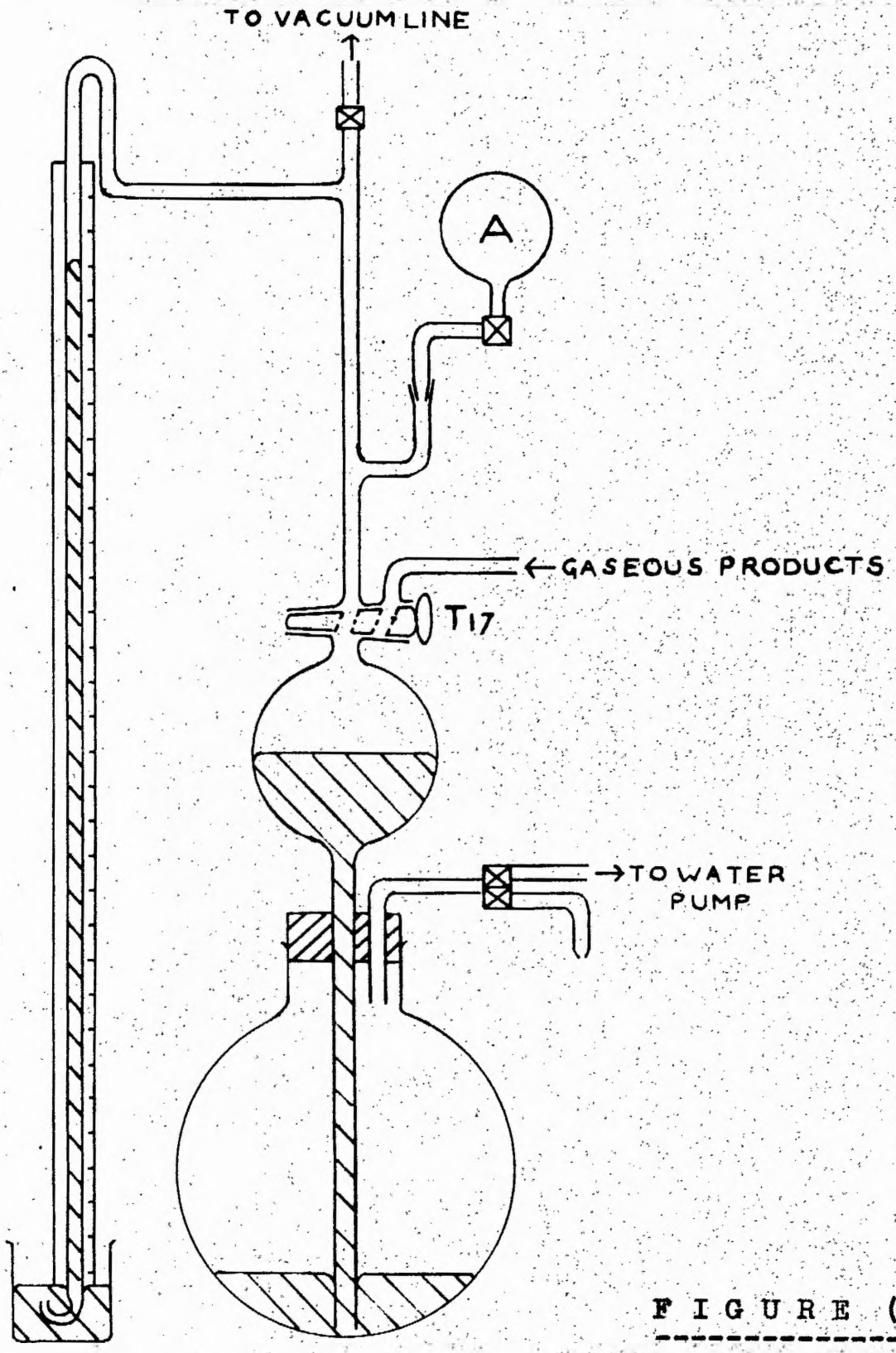


FIGURE (8).

see Table IV.

Furnace.

This was made from an inconel tube 24 inches long and 2 inches in diameter. The tube was covered with asbestos paper, then a layer of Alundum cement approximately one-eighth inch thick. The furnace was wound with 2 mm. Nichrome tape in five sections, with tappings taken off at each section. The winding was covered with another layer of Alundun cement approximately one-quarter inch thick and, finally, with asbestos steam pipe lagging one inch thick.

The resistance of the winding was 40 ohms; this was connected in series with two variable resistances across the power supply, which was obtained from three step down transformers (240 - 115 volts) connected in series.

The furnace temperature was kept constant by means of a Sunvic furnace controller type R.T.2, which operated by proportional control using a platinum resistance thermometer. The furnace and controller circuit was as in Fig.(9), the two variable resistances being available to regulate the basic supply, and the percentage on time of the furnace. The temperature was measured with a chromel-alumel thermocouple, in conjunction with a Pye 35 millivolt Junior potentiometer. The millivolt to ^{o}C conversion tables used were those of

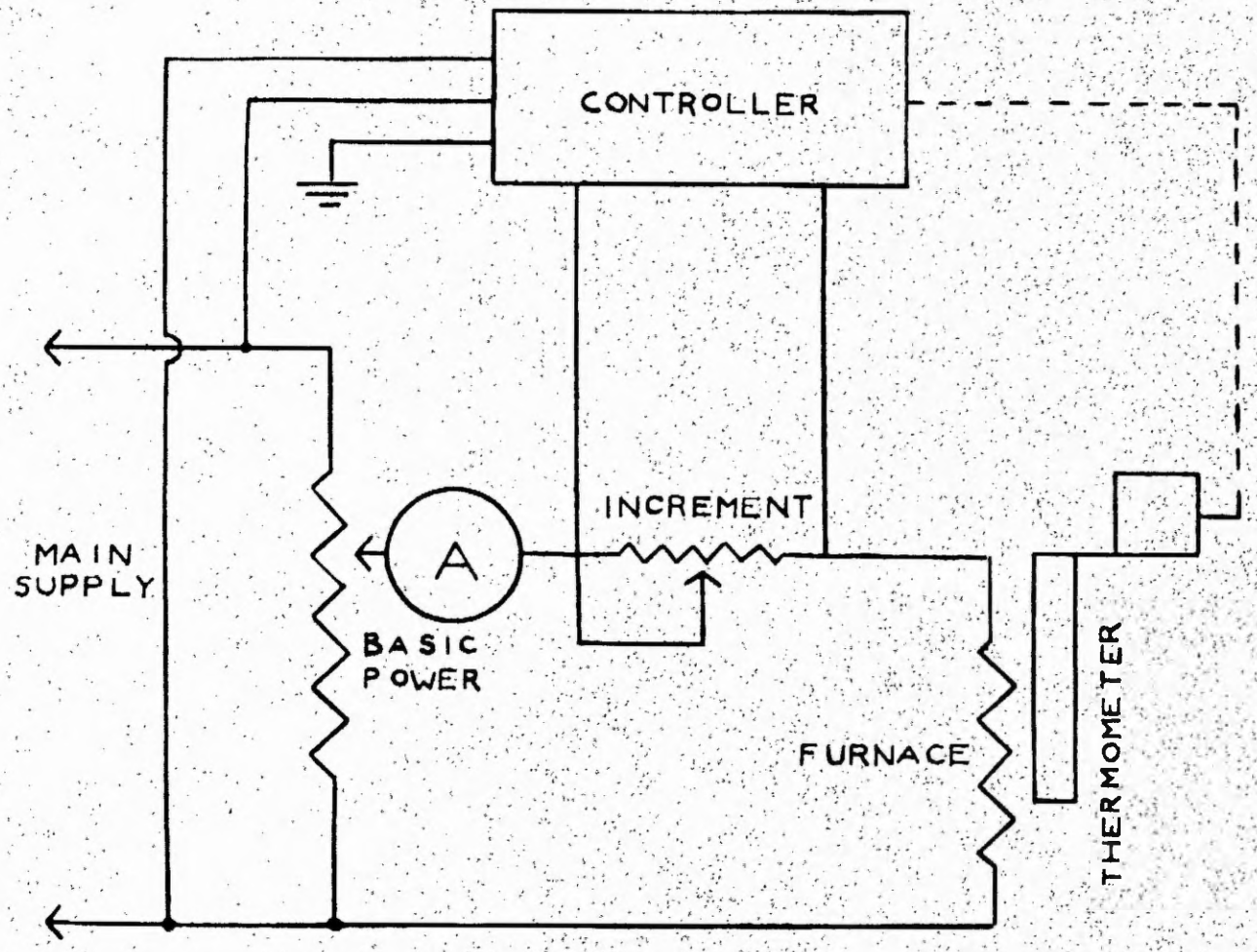

CONTROLLER
MAIN SUPPLY
A
BASIC POWER
INCREMENT
FURNACE
THERMOMETER

FIGURE (9).

Roeser, Dahl and Gowens[39], and the calibrations were checked for the thermocouple used by cooling curve standardisations using aluminium, silver and zinc.

Temperature variations along the length of the furnace were reduced to $\pm$ 2°C by connecting variable resistors in parallel with the sections of the furnace winding. These could be used to reduce the current through a particular section of the winding, and so lower the temperature in that part of the furnace. The process of levelling the furnace was aided by drawing temperature profiles, as in Fig.(10) at various stages.

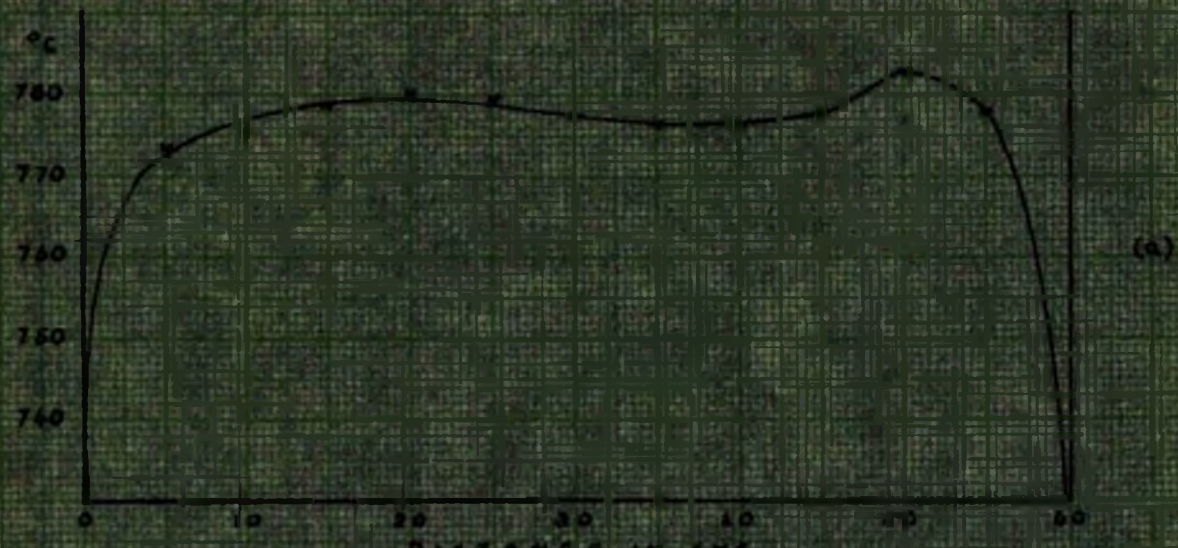
Reaction Vessel.

The reaction vessel was made from wide bore transparent silica tubing, with 12 mm. tubing sealed to each end, and contained a central thermocouple pocket. The narrow tubing was used so that errors due to the slow warming up and cooling down of the reactants were reduced as far as possible. The silica tubing was joined to the rest of the apparatus by graded silica to pyrex seals. The volume of the hot zone of the vessel was 291 ml.

Injection Valves.

The toluene and fluorene were injected into the flow

(a) Preliminary Adjustment



(b) Final Adjustment.

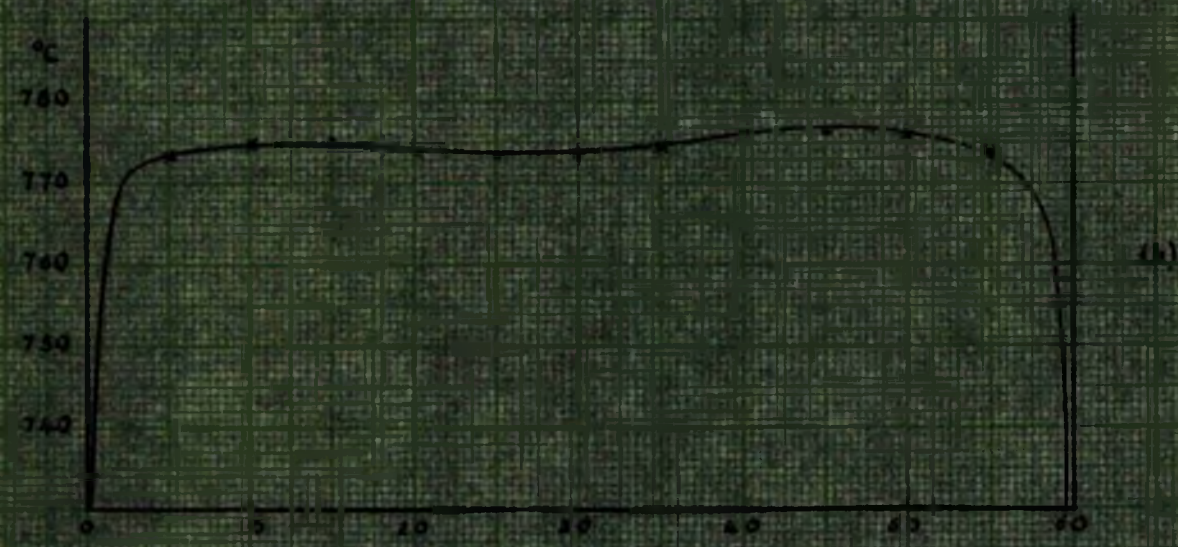


FIGURE (10).

system through two similar valves which were constructed mainly from mild steel and connected in series. The construction of these valves is shown in Fig.(11).

The valve seats were made from copper rod hard soldered on to the steel block, and rounded to fit the 5/16 inch stainless steel balls with which the valve stems were terminated. Stainless steel bellows were originally used to enable the valves to be opened and closed, but the bellows available in stainless steel were not seamless, and since several of these developed leaks down the seam, it was decided to use seamless brass bellows (Power Flexible Tubing Company Catalogue No.112). These proved to be more satisfactory.

"Easy-flo" silver solder was used to join all parts of the valve except those directly attached to the block, when hard silver solder was used. This enabled side arms, etc. to be attached without loosening the original joints.

To prevent twisting of the bellows when opening the valve, 6 B.A. screws were placed in the brass pieces soldered to the tops of the bellows, and the heads of these screws ran in slits cut in the outside valve covers. This arrangement effectively resisted torsional forces on the bellows.

At first, glass capillaries were used to regulate the

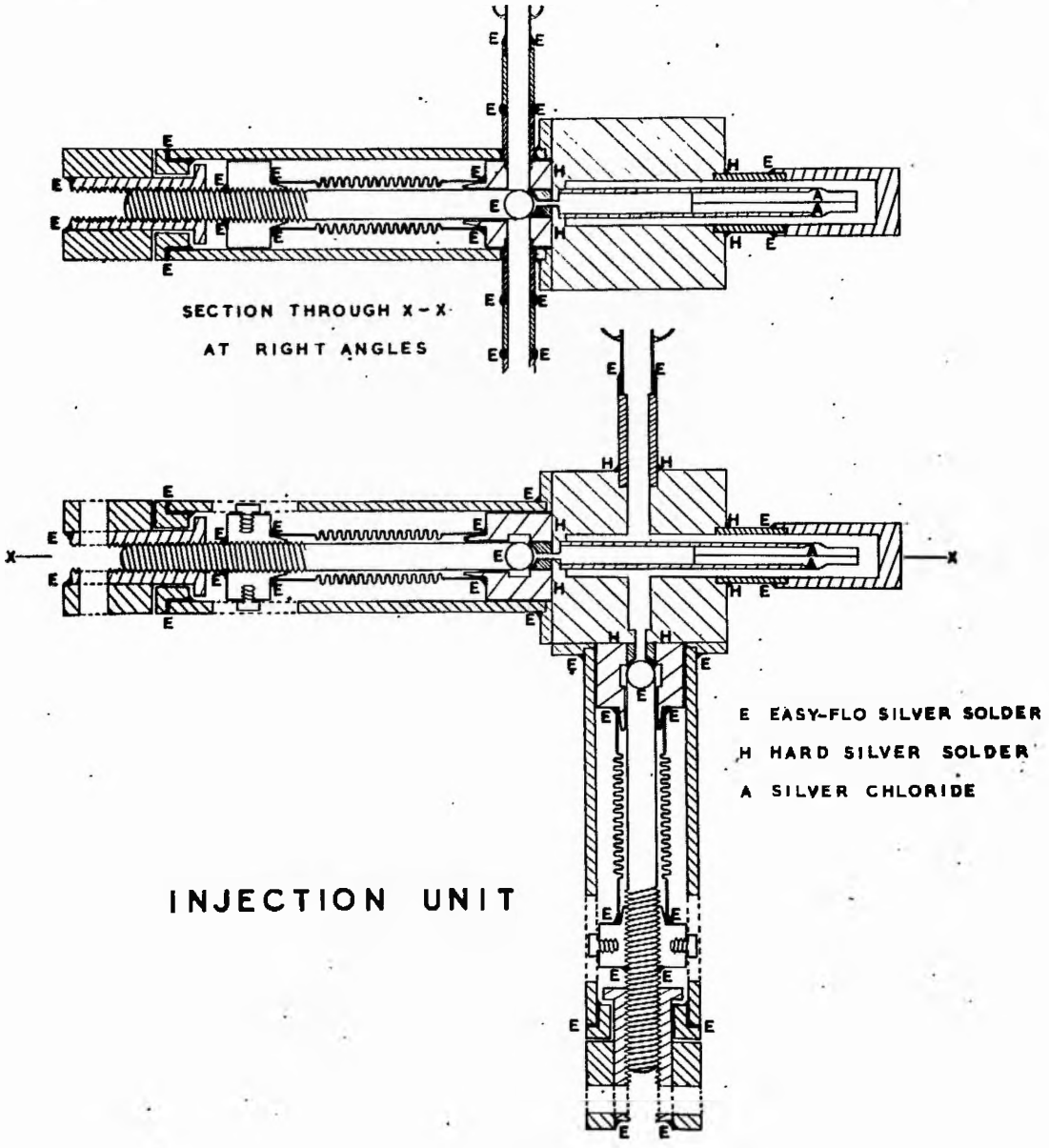

SECTION THROUGH X-X
AT RIGHT ANGLES
E EASY-FLO SILVER SOLDER
H HARD SILVER SOLDER
A SILVER CHLORIDE
INJECTION UNIT

FIGURE (11).

flow of material through the valves. These were made from pyrex capillary tubing with a constriction to give a suitable rate of flow, and were sealed into the valve with fused silver chloride. Later, metal capillaries were used as it was found very difficult to remove the glass ones if they became blocked, or if a different size was required. These were made from brass rod through which a one-eighth inch hole had been drilled. A piece of copper tubing 0.008 inch internal diameter was hard soldered into one end of the brass tube, the length of this tubing being varied according to the resistance to flow required. The resistance to the flow of gases produced by the valve capillaries was measured in arbitary fashion by attaching them to the air inlet on the vacuum line of the main apparatus, and sealing the other end with rubber tubing and a clip. The vacuum line and gaseous products system were evacuated, and air was allowed to leak into this volume through the capillary under test. Readings were taken on the manometer at suitable time intervals, and a graph of the rate of growth of pressure prepared. Intercomparison of capillaries was made easier by this technique, and permitted a suitable one to be selected for sealing into the valves.

The flow sides of the two valves were joined together

using quarter inch internal diameter copper tubing, and a small brass bellows. If the bellows was omitted and a straight tube used, the unequal thermal expansion of the steel and copper tubing strained the joints of the side arms to the main body of the valve, and leaks developed. The vacuum sides of the valves were also joined by copper tubing and connected to a common lead to the vacuum line. The metal to glass seal was made by turning a B.14 cone in brass, hard soldering this to the copper tubing, and sealing the brass cone to a B.14 pyrex socket with Picein wax.

The two valves were joined together by soldering a piece of three-quarter inch iron bar to each, and supported by a framework which could be screwed to the bench and to the wall at the back of the bench. This arrangement was perfectly rigid, and no trouble was experienced from breaking metal to glass seals when opening and closing the valve.

It was necessary to heat the valves to prevent the fluorene from condensing out and, therefore, the cases covering the bellows, the caps over the capillaries, the tubes leading to the injection reservoirs, and the bar joining the valves were covered with asbestos paper and then wound with 2 mm. Nichrome tape. The heater on the connecting bar dissipated 100 watts, and that on the rest of the valve 170

/watts

watts; the power being obtained through a multi-tap transformer. The temperatures of the valve bodies were measured by copper-constantan thermocouples screwed to each, and also attached to directly calibrated temperature indicating meters.

A glass injection reservoir was joined to the fluorene valve by a graded glass to Nilo-K seal, and the reservoir was cut off and glassblown on when it required filling. The toluene reservoir could be removed using a B.14 joint, which was sealed with Edwards W.6 wax. The outside of the joint was covered with Picein wax because it was found that the W.6 wax did not remain vacuum tight when exposed for long periods to the hot water bath which surrounded the reservoir when the toluene was being injected.

Constant Temperature Baths for Injection Reservoirs.

The toluene and fluorene were injected into the system at constant vapour pressures determined by the temperatures of the baths surrounding the reservoirs.

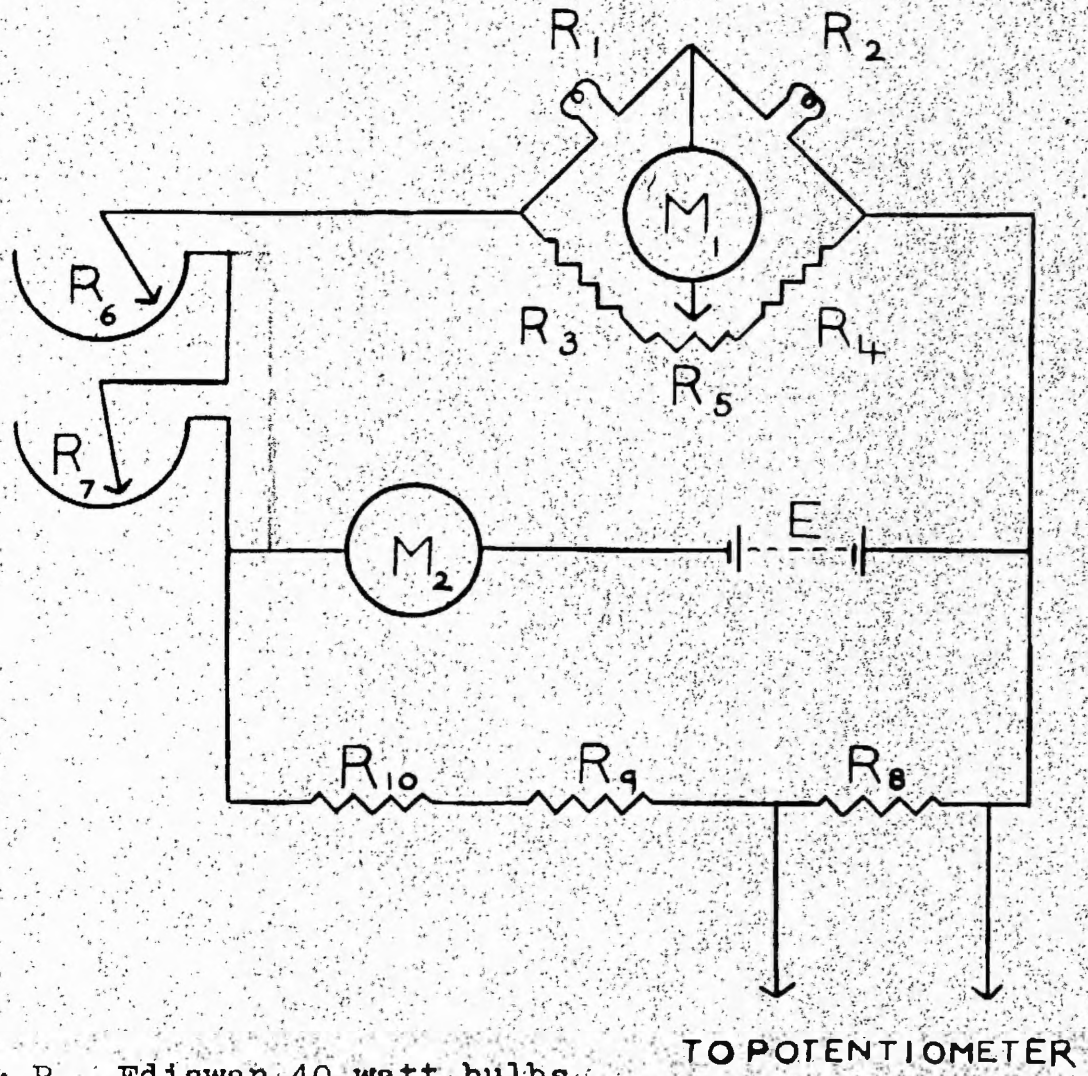
The toluene reservoir was surrounded by a small water thermostat, in which the heater element was a coil of Nichrome wire enclosed in a glass tube, and the temperature sensitive element, a bimetal cartridge type thermo-regulator made by Electromethods, Ltd., Type 318. During use, the bath was stirred vigorously.

The fluorene reservoir was surrounded by an oil bath of similar construction to the water bath, and the temperature was controlled by a Sunvic thermostat, Type T.S.1.

Thermal Conductivity Gauge for the Measurement of Hydrogen.

For reasons which are described later, a method was desirable for the continuous observation of the hydrogen production during a run, which would not interfere with any of the experimental conditions. Since the thermal conductivities of nitrogen and methane are only 14% and 18.5% of the value for hydrogen, it was decided that a gauge based on this property would meet the experimental requirements, since the passage of the carrier gas and products over a heated wire would not, for example, produce any change in the rate of flow, and the lowering of the temperature of the wire and hence the change in its resistance produced by the passage of hydrogen, could be measured with a suitable bridge circuit.

The gauge was constructed from an Ediswan squirrel cage 40 watt light bulb, resistance when cold 120 ohms. The bulb was opened at the bottom and near the top, and B.14 soda glass cones attached. The bulb was included in the flow system as shown in Fig.(3) using Picein wax to seal the glass joints, and could be isolated from the system by two taps T_7 and T_8.



R_1 & R_2	Ediswan 40 watt bulbs.
R_3 & R_4	420 ohm.
R_5	200 ohm wire wound potentiometer.
R_6	1 ohm wire wound potentiometer.
R_7	5 ohm wire wound potentiometer.
R_8	3 ohm.
R_9	550 ohm.
R_{10}	4000 ohm.
M_1	Pye Scalamp galvanometer.
M_2	Milliammeter f.s.d. 120 m.a.
E	12 x 2 volt accumulators.

F I G U R E (12).

A similar bulb was opened at the bottom only, and also joined into the flow system through B.14 joints and a tap T_9. These bulbs were included in a Wheatstone bridge circuit as shown in Fig.(12), the second bulb being used as the compensating resistance R_2.

When in use, the compensating bulb was filled with nitrogen to the same pressure as the flow system, and then tap T_9 was closed. The carrier gas was allowed to circulate through the gauge bulb, and the bridge was balanced by means of the 300 ohm potentiometer R_5. The current through the bridge could be set at a constant value each day by means of the potentiometers R_6 and R_7. As the hydrogen was made during an experiment, the resistance of the gauge bulb changed, and the bridge became unbalanced thus causing a deflection of the galvanometer, so a graph of the galvanometer deflection in centimetres taken at minute intervals during the course of a run enabled the build up of hydrogen to be followed. By injecting known quantities of hydrogen into the flow system from a gas burette, and noting the deflections produced, it was shown that the size of the deflection was directly proportional to the amount of hydrogen in the system. Calibration graphs produced by this method at the end of a series of experiments enabled the technique to be used for the quantitative analysis of hydrogen, and are shown in Fig.(13).

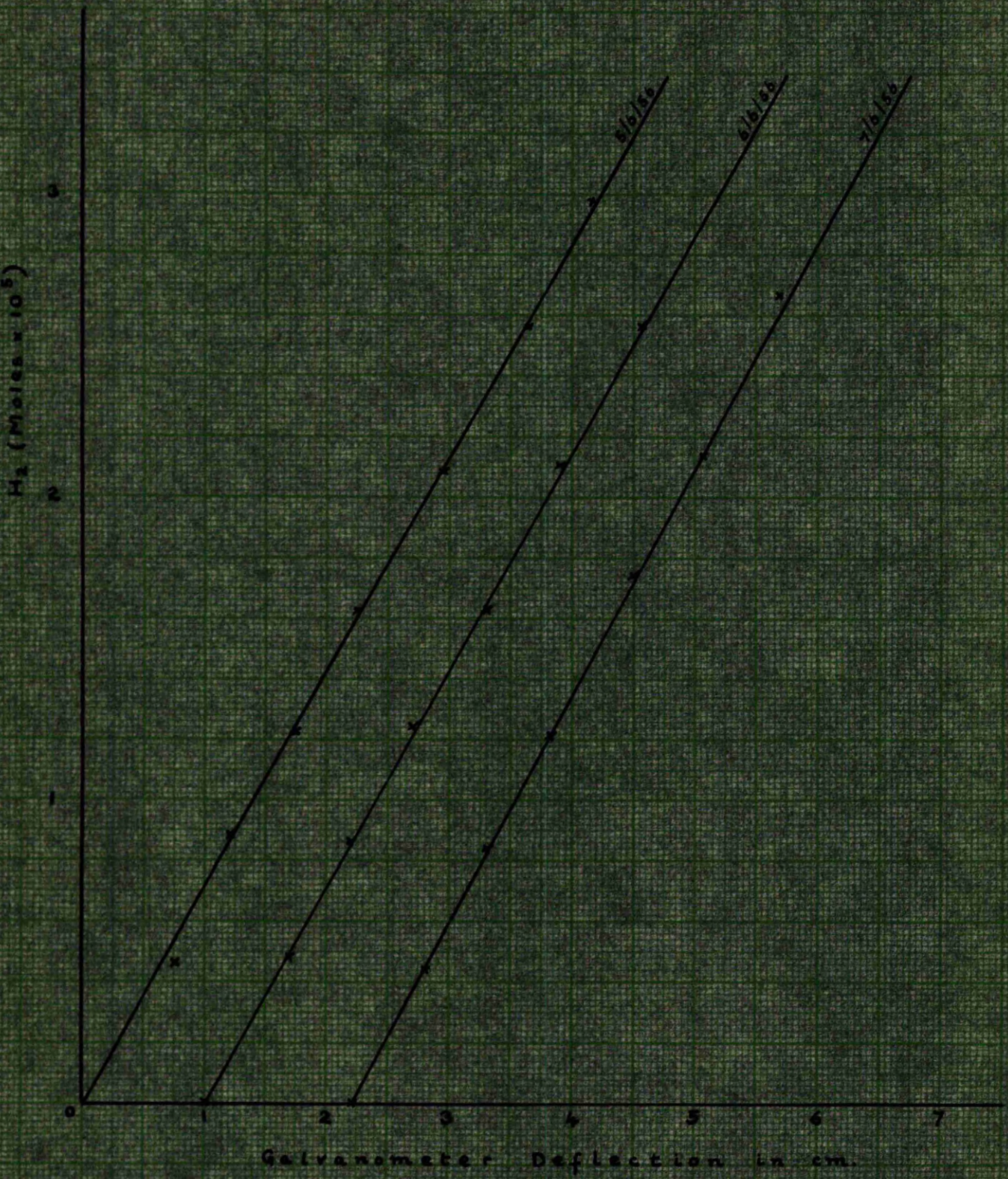

5/b/56
6/b/56
7/b/56
H_2 (Moles x 10^5)
0
1
2
3
1
2
3
4
5
6
7
Galvanometer Deflection in cm.

FIGURE (13).

When first used, the galvanometer reading was very unsteady; This was found to be due to four imperfections in technique listed below.

(1) In the original form of the apparatus, the voltage across the bridge was supplied from the mains via a constant voltage transformer and rectifier, and this was not found to be sufficiently steady. An improvement was effected by connecting an 85A1 voltage stabiliser tube across the output, with associated resistances, but this was still unsatisfactory, and finally, twelve two volt accumulators were employed. Provided that these were not used immediately after charging, the voltage remained very steady, and, in practice, the bridge was allowed to stabilise by connecting the batteries about half an hour before the gauge was required.

(2) The variation in temperature of the glass bulbs containing the gauge and compensating resistances had an appreciable effect on the galvanometer zero. To prevent this, both bulbs were immersed in a bath of constantly flowing tap water when the gauge was in use. After running the water for some time, the temperature was found to vary by only about one degree centigrade during the course of a series of experiments, and this did not affect the stability of the gauge.

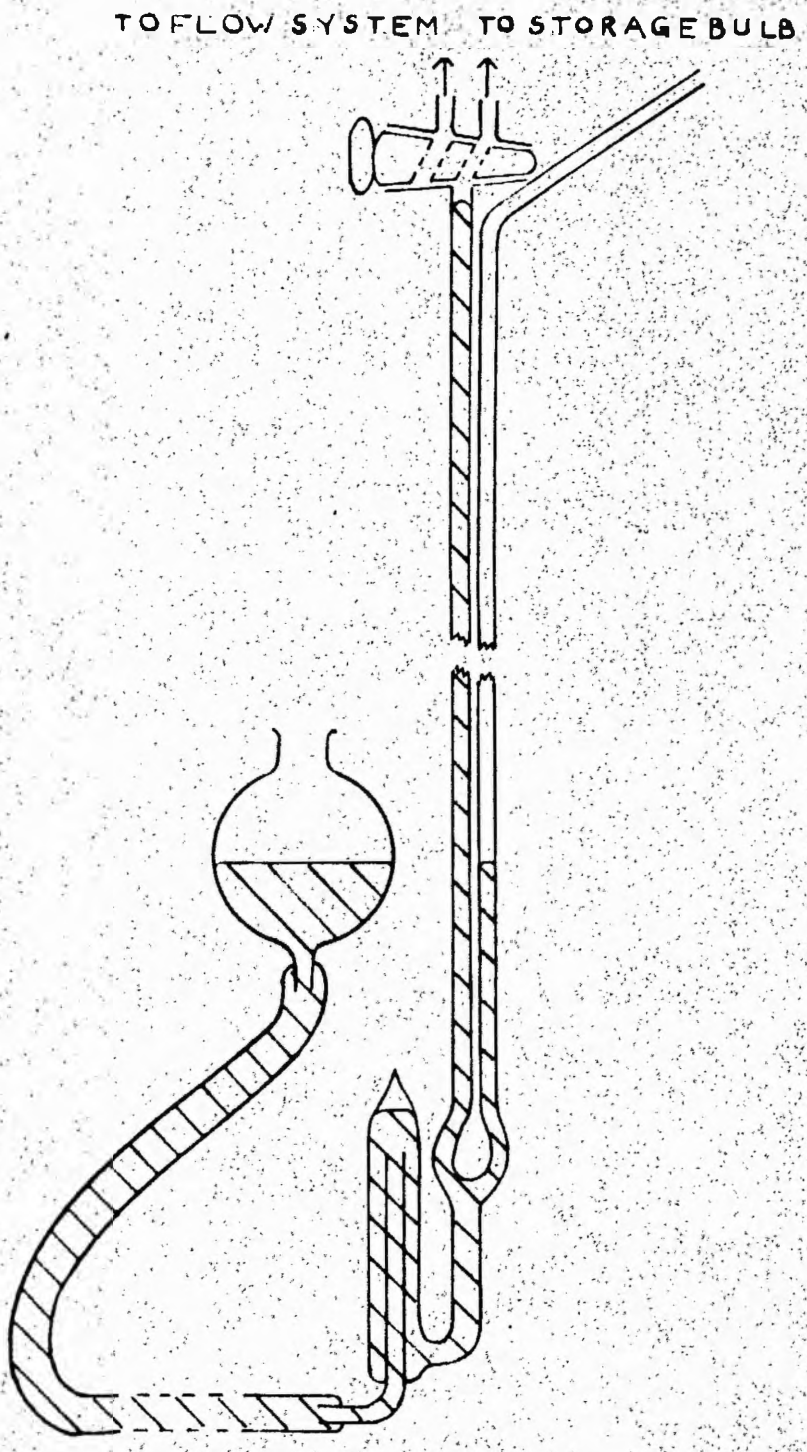


FIGURE (14).

(3) The constancy of the rate of flow of the carrier gas proved to be an important factor, and this could be readily checked by stopping the circulation of gas through the gauge when stable behaviour would be observed if all other factors were constant. It was, therefore, important to see that the circulation pump was working under the best conditions, and that the stem of the pump was heated.

(4) Evaporation of refrigerant from the baths placed round the traps in the flow system was found to cause a rise in total pressure sufficient to cause a drift in the bridge zero. To prevent this, the baths were filled up every few minutes during the course of an experiment.

The Gas Burette for Hydrogen Calibrations. (Fig.14)

The gas burette was constructed from nominal 2⅔ mm. internal diameter tubing. The calibrated section was a piece of uniform bore with radius 1.3 mm., and was graduated in lengths corresponding to 0.1 ml. Before sealing the calibrated tube to the compensating tube it was joined to the two-way tap, then filled to a known position with mercury, the amount required being weighed so that the volume of the tube between the tap and the start of the uniform bore tubing could be determined. This volume was 0.44 ml. The burette was filled from a flask of pure hydrogen joined to one arm of the two-way tap, the other arm leading to the flow system. The

pressure of gas in the burette was obtained by subtracting the difference in level of the mercury in the burette and compensating tubes from the atmospheric pressure; since the initial and final pressures and volumes of hydrogen were known together with the laboratory temperature, the number of moles of gas injected could be calculated.

Copper Oxide Furnace.

When it was desired to conduct a series of runs without change of carrier gas, or possible alteration of wall conditions in the reaction vessel, it became necessary to combust the gaseous products and remove them from the circulating gas. If this was not done, the determination of further hydrogen production by the thermal conductivity gauge became inaccurate since the galvanometer shunt had to be operated to provide a coarse range in order to accommodate the larger readings. Alternative electrical arrangements could, of course, have been made to deal with this, but since it was undesirable to have a change in the nature of the carrier gas, it was thought preferable to introduce a copper oxide furnace into the circuit.

The furnace was a 6 inch length of 15mm. tube packed with wire-form copper oxide, and was heated to 300°C by a

Nichrome winding, the products being removed in a U-tube cooled in liquid air.

PREPARATION AND PURIFICATION OF MATERIALS.

GASES.

Nitrogen.

The nitrogen used was supplied by the British Oxygen Company, and was purified by passing it through a trap cooled in liquid air and then through a sodium trap to remove any oxygen present.

Helium.

This was purified by the same method as for the nitrogen.

Methane, Ethane and Ethylene.

These were standard samples for mass spectrometry obtained from the Chemical Research Laboratory, Teddington.

Hydrogen.

Hydrogen supplied by the British Oxygen Company was purified before use by passing it through a heated palladium thimble.

Deuterium.

The deuterium was prepared by the electrolysis of heavy sulphuric acid.

(A) Preparation of D_2SO_4.

Sulphur trioxide was prepared by the distillation of fuming sulphuric acid[40], special precautions being taken to free the material from water, and then distilled into heavy water.

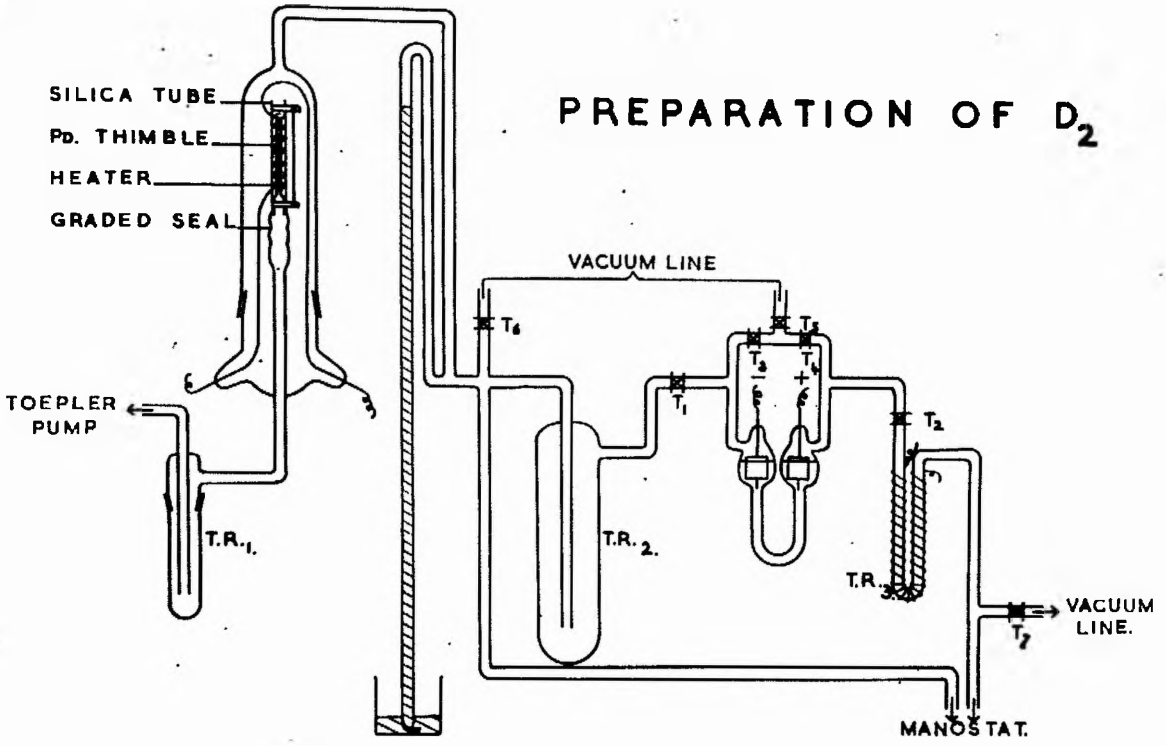
The trial apparatus consisted of a two-necked round bottomed flask, one neck being closed by a B.14 stopper and the other sealed to a U-tube, filled with phosphorus pentoxide, followed by a trap; this sequence was repeated twice and the train ended with a fourth trap. The last two traps were separated from the rest of the apparatus and from each other by three taps. The flask was half filled with fuming sulphuric acid and sulphur trioxide was distilled into the first trap which was surrounded by a bath at $-80^{\circ}C$. The flask of acid was removed by sealing off the connecting tube, and the apparatus evacuated. The solid sulphur trioxide was then distilled into the second trap, through the phosphorus pentoxide, the bath around trap (1) being at $-40^{\circ}C$, and that around trap (2) being at $-185^{\circ}C$. The process was repeated until the sulphur trioxide had been distilled into the fourth trap.

The sulphur trioxide from this experiment was a waxy solid which did not easily melt, and was evidently contaminated by decomposition products of the silicone grease used on the

FIGURE (15).

taps. To prevent this, it was decided to construct an apparatus with no taps in the vicinity of the sulphur trioxide, as shown in Fig.(15).

The U-tubes (A), (B) and (C) contained a mixture of phosphorus pentoxide and glass wool, the latter prevented close packing of the powder from slowing down the distillation. The flask was filled with fuming sulphuric acid as before, and the side tube was sealed off. Sulphur trioxide was distilled into the first trap and the flask sealed off. Liquid air baths were placed round traps (1) and (2), and the apparatus evacuated and sealed off from the pump. The solid sulphur trioxide was distilled into trap (2) by allowing trap (1) to slowly warm up to room temperature; the process was repeated to distil the material into trap (3). At this stage, needle like crystals were obtained as opposed to the waxy solid obtained in the trial experiment. The solid was distilled back into trap (2), then sufficient to give approximately 1 ml. liquid sulphur trioxide distilled into trap (3), this being the quantity required to give a 30% by weight solution of D_2SO_4, this strength of solution having a higher conductivity than any other. Trap (3) was sealed off from the rest of the apparatus, then joined on to a small flask of water cooled in ice. The internal seal on trap (3) was broken, and the sulphur trioxide warmed gently to distil it into the


PREPARATION OF D_2
SILICA TUBE
Pd. THIMBLE
HEATER
GRADED SEAL
VACUUM LINE
TOEPLER PUMP
T.R.1.
T.R.2.
T.R.3.
T_1
T_2
T_3
T_4
T_5
T_6
T_7
VACUUM LINE.
MANOSTAT.

F I G U R E (16).

water. The experiment was repeated, the sulphur trioxide being distilled into 99.75% D_2O and the flask of D_2SO_4 sealed off until required.

(B) Preparation of Deuterium.

The main problem in the construction of an apparatus for the electrolysis of a solution of heavy sulphuric acid, centres on the necessarily small size together with the production of two volumes of deuterium to one volume of oxygen by the electrolysis; this latter point makes it difficult to keep the acid levels the same on both sides of the cell. It was also desired to make an apparatus that would require as little attention as possible when working, and that would produce the required amount of gas in a reasonable time. These points have produced several solutions by different authors, and the equipment suggested by Winn[41] and Lloyd[42] was adopted as a general guide.

The electrolysis cell was constructed from pyrex glass, as in Fig.(16). Two bulbs of approximately 8 ml. capacity were sealed to a 2 mm. diameter bore U-tube approximately 4 cm. long. The electrodes were made from platinum foil spot-welded to platinum wire, and these were silver soldered to tungsten wires which were sealed into the bulbs. The taps (1), (2) and (5), enabled the cell to be completely

isolated from the rest of the apparatus, and taps (3) and (4) were used when evacuating the apparatus and, if necessary, to equalise the pressure in the two halves of the cell.

The deuterium was purified by passing it through a heated palladium thimble, and this piece of the apparatus was made in a similar manner to that of Winn[41]. The pyrex lead from the cathode compartment of the cell conducted the gas through a trap $T.R._2$ to remove moisture, and into the envelope around the palladium thimble. At a T-junction in this line, one side of a manostat was connected. The palladium thimble was 2 mm. diameter and 4 cm. long, and was soldered with gold into a slightly larger platinum tube, which in turn, was hard soldered into a Nilo-K tube. This was then connected by a graded glass to pyrex seal through the bottom of the enclosing envelope to the purified deuterium handling and storage equipment. The thimble was heated by a coil of 0.020 inch diameter Nichrome wire wound inside a silica tube. This tube was supported by a clip and rod attached to the Nilo-K tube. The heating current was led through the glass envelope to the Nichrome coil by tungsten wire seals, and these were hard soldered to flexible nickel leads. A satisfactory rate of diffusion through the thimble was obtained when the heater was dissipating 90 watts.

Deuterium which diffused through the palladium thimble

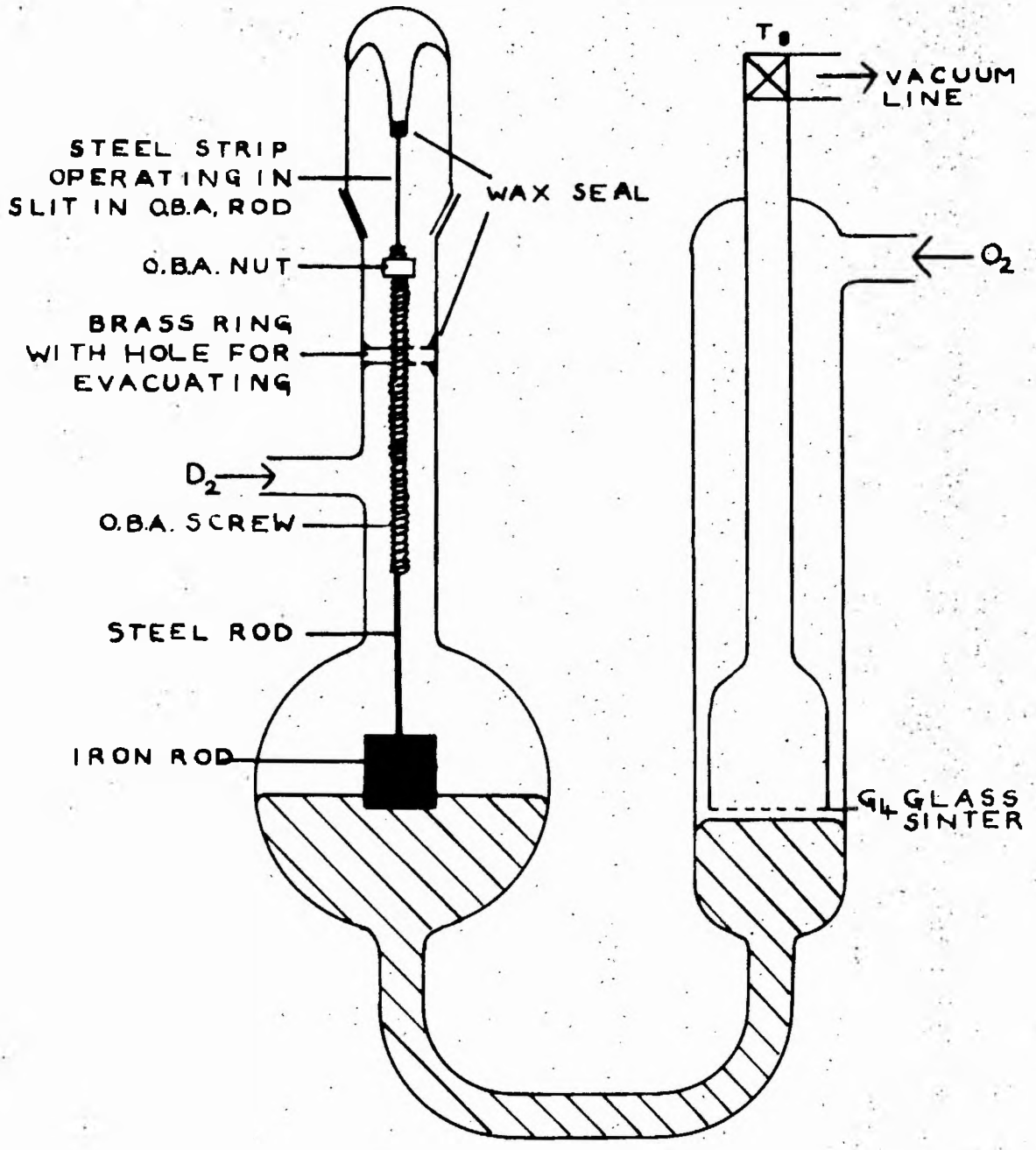

T8
VACUUM LINE
STEEL STRIP OPERATING IN SLIT IN O.B.A. ROD
WAX SEAL
O.B.A. NUT
O2
BRASS RING WITH HOLE FOR EVACUATING
D2
O.B.A. SCREW
STEEL ROD
IRON ROD
G4 GLASS SINTER

FIGURE (17).

passed through a small trap, T.R.$_1$, into a Toepler pump of capacity 500 ml., and was then forced into a three litre storage bulb. The purpose of the small trap was to catch any mercury spilled over in the direction of the palladium thimble during the operation of the Toepler pump.

The deuterium and oxygen sides of the cell were connected on the far sides of taps (T_1) and (T_2) to a manostat, which was a modification of the apparatus used by Lloyd.[42] The manostat is required to cope with the fact that the volume of the deuterium side of the apparatus cannot easily be made exactly double that of the oxygen side and, therefore, pressure differences occur which cause the electrolyte seal between the anode and cathode compartments to be destroyed; the same effect was produced by the expansion and contraction of the deuterium which occurred on warming and cooling the palladium thimble. The manostat was constructed as in Fig.(17). The mercury level could be adjusted by raising or lowering the piece of three-quarter inch iron rod by means of the screw thread and driver fitted in the B.24 stopper. The oxygen was pumped away through the G.4 glass sinter using the rotary oil pump attached to the main apparatus. The gases entered the manostat above the mercury on each side as shown in the diagram, and by adjusting the height of the mercury below the sinter by means of the screw, it was possible

to keep the acid levels in the cell the same.

The following considerations apply to the state of the acid levels in a cell of this type when working:-

(1) When the palladium thimble is cold, if the volume of the free space on the deuterium side of the apparatus is greater than twice that on the oxygen side, then the pressure of deuterium will be less than that of the oxygen, and the acid level in the cell will rise on the deuterium side; but, in these circumstances, the excess oxygen will be withdrawn through the sinter on the manostat, until the levels are equalised. If the volume of the deuterium side is less than twice that of the oxygen side, the pressure of deuterium will be greater than that of the oxygen and the level of the acid will fall on the cathode side of the cell until the electrode is exposed, when the electrolysis will cease until readjustment of pressure is obtained by heating the thimble and allowing the deuterium to diffuse through.

(2) With the thimble hot, there is the extra factor of the rate of permeation of the palladium thimble by the deuterium to be considered. If permeation is faster than electrolytic generation, the equalisation of pressures has to be done entirely by the removal of oxygen through the manostat sinter. If electrolytic generation is faster than permeation, the precise operation depends on the relative volumes of the oxygen

and deuterium sides of the cell as described in (1).

As shown, the arrangements made were capable of continuous control of the electrolytic process for any set of experimental circumstances.

When first set up, the connection from the manostat to the oil pump was made with a piece of rubber tubing. This perished extremely rapidly when the cell was in use, and the mercury on the oxygen side of the manostat became very dirty. It was thought that this was caused by ozone formed during the electrolysis, and it was found that if the gas was passed through a U-tube, T.R.$_3$. heated to about 420°C, no further trouble was experienced.

Trial experiments were done with the apparatus using 30% sulphuric acid and then the 30% heavy sulphuric acid, as prepared on page 68 was used.

Description of Method of Use of the Apparatus.

First the apparatus was completely evacuated, freezing the electrolyte by surrounding the cell with a liquid air bath, and degassing the palladium thimble and ozone trap T.R.$_3$ by heating under vacuum for several hours. All taps to the vacuum line, T_5, T_6 and T_7, with the exception of T_8 on the manostat were closed, and electrolysis commenced. It was necessary to surround the cell with a bath of constantly flowing cold water, because the electrolyte became very hot;

and initially only a very low current could be passed because of considerable frothing of the electrolyte due to the low pressure in the apparatus. Once the gas pressure had been built up, the cell could be run very smoothly off 60 volts. The variable voltages required were obtained by connecting a selenium rectifier across the required tappings on a multi-tap transformer.

The screw on the manostat was adjusted until the acid levels in the cell remained steady, and once frothing of the electrolyte had ceased the apparatus required no further attention, apart from occasionally pumping the purified deuterium into the storage bulb.

To shut down the apparatus, taps T_1 and T_2 were closed, then the electrolysis stopped, tap T_8 on the manostat closed, and the heaters for trap T.R.3 and the palladium thimble switched off.

To re-start the preparation after shutting down in this way, the thimble and trap heaters had to be put on, tap T_8 opened to the oil pump, taps T_1 and T_2 opened with care, and electrolysis commenced. Due to the different solubilities of the gases in the electrolyte, the cell U-tube liquor seal was destroyed when the apparatus was left shut down over night and, therefore, before recommencing electrolysis, the pressures on both sides of the cell had

to be equalised by freezing down the acid and evacuating the cell with taps T_1 and T_2 closed. Taps T_3 and T_4 were shut, electrolysis commenced and taps T_1 and T_2 carefully opened.

LIQUIDS.

Toluene.

Previous work[1] has shown that in order to obtain reproducible results for the pyrolysis of toluene, it is necessary to prepyrolyse the starting material. Petrochemicals reagent grade toluene was placed in a reservoir of about 100 ml. capacity, which was attached to the toluene injection valve. The toluene was thoroughly de-gassed, then partially pyrolysed at 845°C. This was repeated, then the toluene was distilled over sodium using a column, three feet in length, packed with Fenske rings and with a high reflux ratio.

Methanol.

The methanol used for ultra-violet spectroscopic purposes, was purified by refluxing with activated charcoal for three hours, and then distilling. It was not found necessary to dry the alcohol. The optical density of the material purified in this way was not significant above

230 mμ, which was 30 mμ below the wave-lengths used for analyses.

SOLIDS.

Fluorene.[38]

75 gm. fluorene was oxidised to fluorenone by sodium dichromate in glacial acetic acid, the yield being 58 gm.. 13 gm. of the fluorenone was refluxed for half an hour with 32.5 gm. hydroxylamine hydrochloride in 260 ml. 5% caustic soda solution, and the oxime was recrystallised from ethyl alcohol. The yield was 10.5 gm. and the melting point 190°C.

10 gm. oxime was dissolved in 500 ml. absolute alcohol in a 1 litre round bottomed flask fitted with a reflux condenser. 1000 gm. sodium amalgam was added, and the mixture kept acid by the addition of glacial acetic acid. On completion of the reduction, the mixture was poured into 4 litres of water. The solid product was filtered off, recrystallised from benzene and then from ethyl alcohol, dissolved in benzene and spun in the centrifuge at 2750 r.p.m. for three minutes to remove mercury. The melting point of the fluorene was 114.5 - 115°C. When dissolved in methanol, this material did not show an ultra-violet absorption spectrum at wave-lengths greater than 310 mμ .

4-Methyldiphenyl.[43]

27 gm. p-toluidine was dissolved in 80 ml.(1.16) hydrochloric acid and 45 ml. water, and diazotised with sodium nitrite solution. 250 ml. benzene was added, and the mixture stirred vigorously keeping the temperature between 5 - 10°C. 15 gm. caustic soda in 75 ml. water was added, and the stirring continued for 48 hours, the stirring being at room temperature after the first three hours. The benzene layer was separated, washed with water, and the benzene distilled off. The remaining mixture was distilled under 20 - 30 mm.Hg., the fraction passing between 175 - 185°C being collected. The product was recrystallised from ethyl alcohol and the yield was 22%. Melting point 46°C.

4-4'-Dimethyldiphenyl.[44,45].

(a) Preparation of p-iodotoluene.

25 gm. p-toluidine was dissolved in 275 ml.10% sulphuric acid and the solution cooled to 0°C with stirring to produce small crystals of the sulphate. A solution containing 20 gm. sodium nitrite in 40 ml. water was slowly added, the temperature being kept below 10°C. Then a solution of 60 gm. potassium iodide in 100 ml. water was added, and the stirring continued for one hour at room temperature. Then the mixture was warmed on a water bath until

effervescence ceased, and steam distilled. The p-iodotoluene solidified in the receiver as a yellow solid and was purified by recrystallisation from alcohol. The yield was 33%, and the melting point 35°C.

(b) Preparation of 4-4'-dimethyldiphenyl.

5 gm. p-iodotoluene was heated to 210°C, and 5 gm. copper bronze powder added slowly. The mixture was cooled and the product extracted with absolute alcohol. The crude material was recrystallised from alcohol. Melting point 120°C.

Dibenzyl.[11]

A sample of dibenzyl was used which had been purified by recrystallisation followed by reduction to eliminate stilbene, the reduction being continued until no stilbene was observed in the ultra-violet spectrum of the material. Melting point 52.5°C.

Diphenylmethane.[32]

The sample used had been purified by vacuum distillation collecting the fraction boiling under a pressure of 12 mm.Hg. and then subjecting this to fractional freezing until a material was obtained which melted at 26.4°C.

Stilbene (trans) and Diphenyl.

These were commercial products purified by re-crystallisation to melting points of 124°C and 69 - 70°C respectively.

ANALYSIS OF PRODUCTS.

GASES.

Two methods were used for the analysis of the gaseous products:-

(1) The thermal conductivity gauge which has been described on page 61 for the analysis of hydrogen, and

(2) the mass spectrometer which was used for the analysis of all gaseous products.

The mass spectrometer was constructed in the department, and is a Nier type with a 60° sector magnet, the resolution being 1 in 200. The masses are scanned by magnetic field variation, this being from zero to 6000 gauss. The ion accelerating voltage ranges from zero to 2000 volts, and both this and the current for actuating the magnet are obtained from electronically stabilised power supplies.

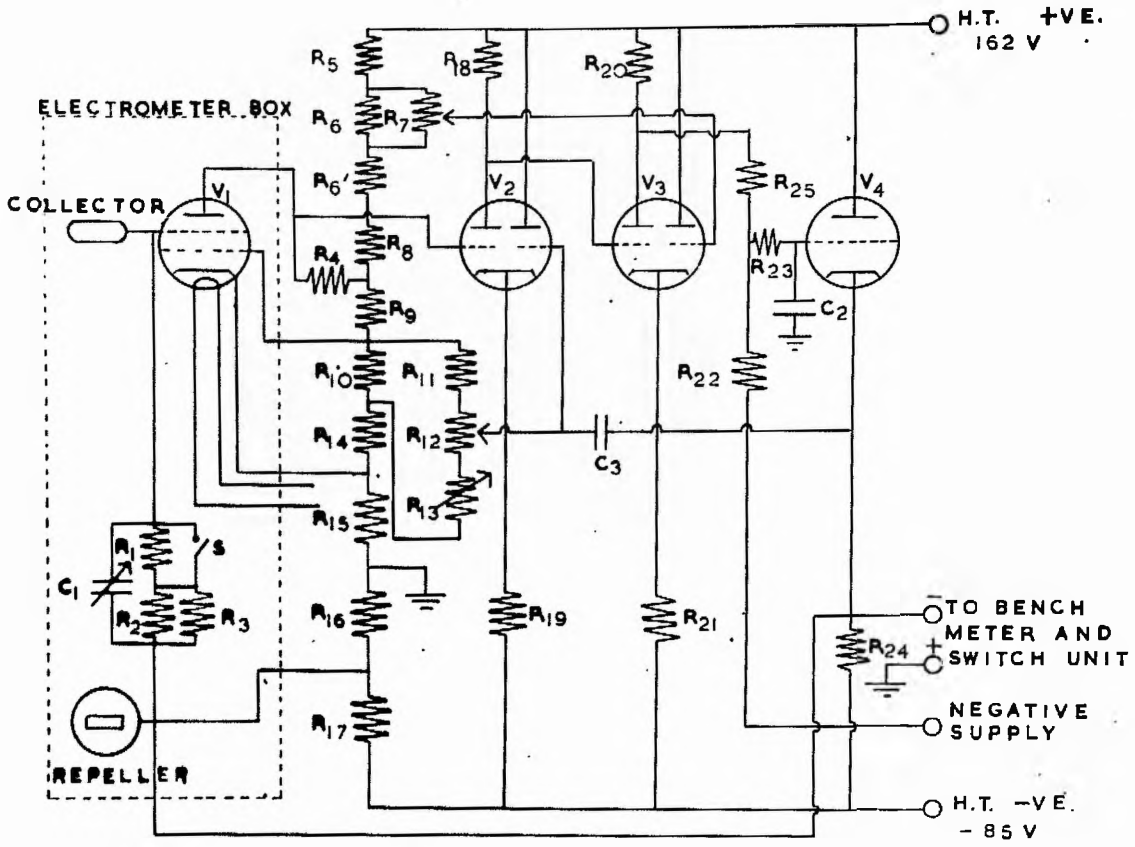
The ion current passes down one of two resistors which have absolute values 2×10^{11} and 3×10^{10} ohms, giving a ratio of 1 : 6.67. The voltage produced is the input for a 100% negative feedback amplifier, the output being connected to a multi-range voltmeter and a Honeywell Brown recording potentiometer. The sensitivity on the high grid resistor is 10^{-14} amps per chart division.

A vacuum of 10^{-6} mm.Hg is maintained inside the instrument by means of a mercury diffusion pump backed by a Metrovac D.R.l. rotary oil pump. When not in use for analysis, the vacuum is maintained by the diffusion pump discharging into a five litre backing bulb.

During the course of the use of the mass spectrometer, a quite inexplicable unsteadiness of the amplifier and recording system was found on some days. Since it was necessary to be able to estimate small quantities of hydrogen and methane in the presence of a large amount of nitrogen, consistent behaviour on the lowest range of peak heights, that is up to 100 mV., and a reasonably stable zero reading were very desirable. In view of the behaviour of the instrument, some work was done to find the causes of the trouble, and two of these were discovered, one being a mechanical matter with electrical consequences, and the other being entirely electrical.

When building the instrument an attempt had been made to isolate the electrometer valve of the D.C. amplifier from vibrations. The ions received on the collector plate in the mass spectrometer tube passed out of the latter along a stiff lead through a well insulated glass seal, then through the 10^{11} or 10^{10} ohm resistor down to earth. The tops of these

F I G U R E (18).



CIRCUIT FOR D.C. AMPLIFIER

V_1	BM8A	R_8	10 K	R_{18}	360
V_2, V_3	12SC7	R_9	1.5 K	R_{19}	200 K
V_4	12J5	R_{10}	560	R_{20}	100 K
R_1	1.79×10^{11}	R_{11}	100 K	R_{21}	100 K
R_2, R_3	5×10^{10}	R_{12}	100 K	R_{22}	3.3 M
R_4	120 K	R_{13}	2 K	R_{23}	100 K
R_5	15 K	R_{14}	510	R_{24}	25 K
R_6	15 K	R_{15}	670	R_{25}	2 M + 470 K
R_6'	15 K	R_{16}	680	C_1	10 pF
R_7	100 K	R_{17}	680	C_2	0.1 μF

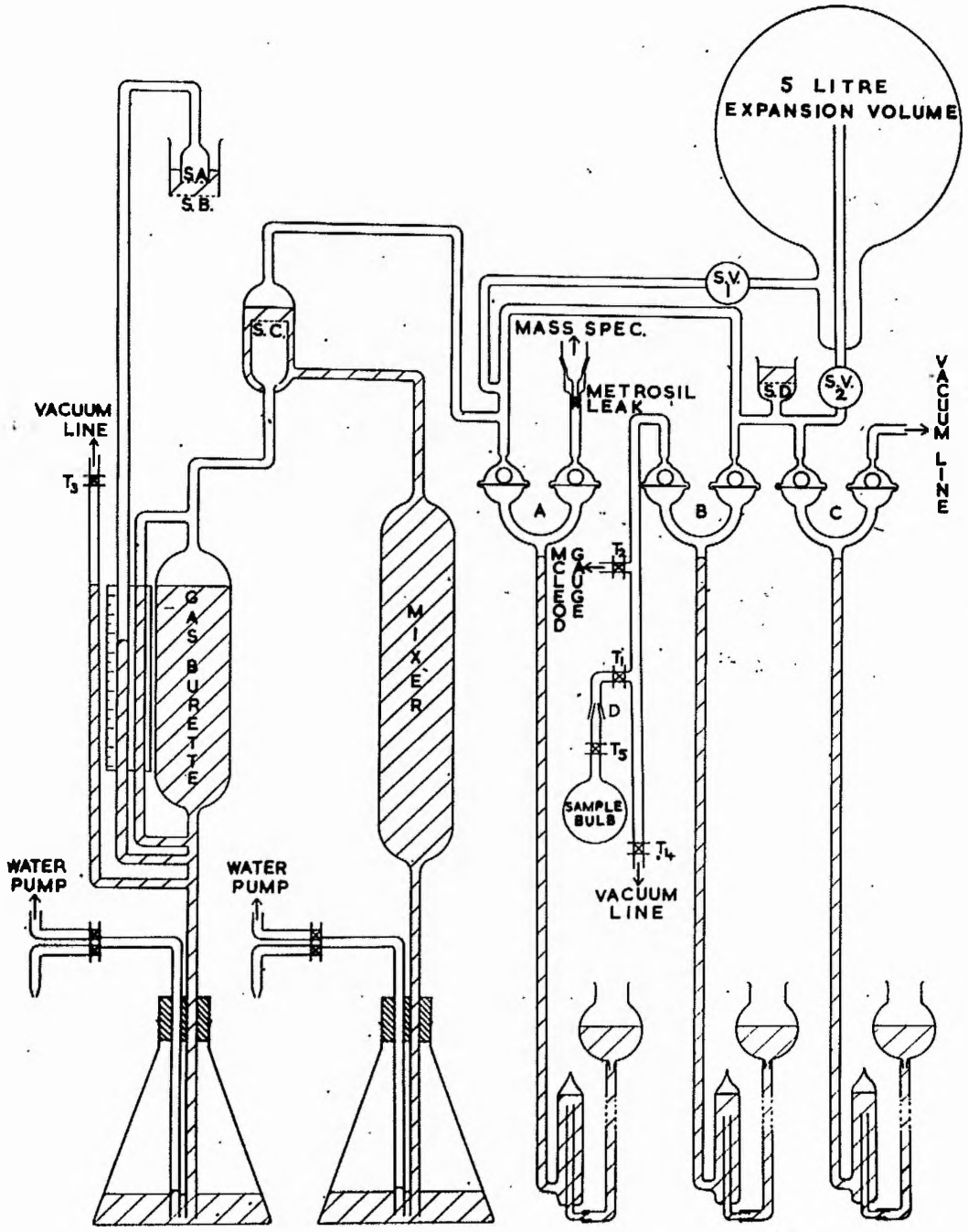
resistors were connected to the grid of the electrometer valve, and the resistors and valve were mounted in a box which was connected flexibly to the end of the mass spectrometer tube. This flexible connection was formed by a thin metallic bellows, through the centre of which the ion collector lead was passed. Tests showed that while this mechanism isolated the heavy electrometer box from vibrations which, although imperceptible might be transmitted via the tube, it caused a worse electrical error by producing a slight change in capacity between the central collector lead and the earthed bellows. This could and did cause a spurious fluctuating potential to be received at the grid of the electrometer valve. The error was removed by suspending the electrometer box directly from the end of the mass spectrometer tube.

The elimination of this fault in the electrometer mounting described above did not cure all the troubles of the amplifier. The circuit for this amplifier is shown in Fig.(18), and as can be seen, is of the 100% negative feedback type using four valves, a Ferranti electrometer [redacted]A, two 12SC7 double triodes and a 12J5 output valve. In such a circuit, the most sensitive places at which disturbances are likely to arise are in the first two valves. Tests at these points failed to disclose any reasonable source of the troubles observed. The associated components were all replaced without

effect, and the valve potentials all appeared to be reasonable. All the valve heaters were supplied from a stabilised power pack, and nothing could be traced to this. An investigation with a valve voltmeter showed that with certain settings of the balancing controls R_{12}, R_{13} and R_7, and with certain applied signals, one grid of the second 12SC7 could be made very slightly positive. This undesirable feature did not prevent the amplifier performance from continuing to be linear up to even higher applied signals. It was concluded, however, that this could be the cause of the unstable behaviour and that it could be aggravated by unsuitable settings of the balancing rheostats. By adjustment of the anode and cathode load resistors, it became possible to operate the second 12SC7 under better conditions of electrode potential and achieve amplifier linearity up to 15 volts applied signal without causing the signal grid to go positive. This produced a marked improvement in the zero stability.

The gases were fed into the mass spectrometer through a Metrosil 4F porous plug leak. This was sealed into pyrex glass by collapsing a tube round the Metrosil under vacuum, since sealing in the ordinary way was not found to be satisfactory because longitudinal leaks formed between the glass and the Metrosil.

The existing gas handling system consisting of a series



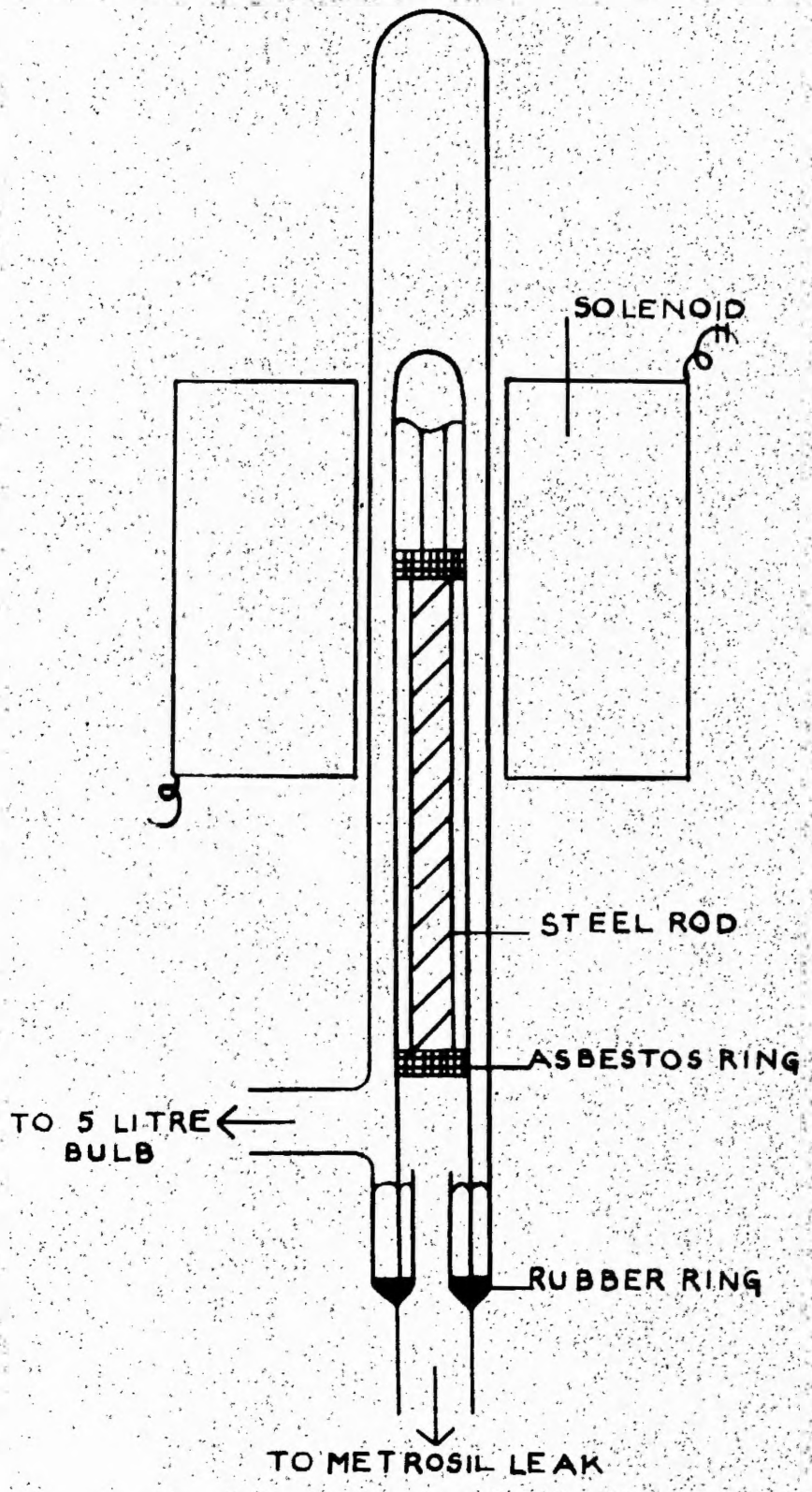
GAS HANDLING SYSTEM

FIGURE (19).

of mercury cut-offs, a Toepler pump used as a mixer, and a five litre expansion volume, which could be isolated from the leak by means of a solenoid valve, was modified by Naylor who used a mercury covered sinter greaseless tap technique for introducing the calibration gases. The final apparatus used is shown in Fig.(19).

The calibration gases were contained in bulbs sealed by G.4 grade glass sinters covered with mercury. To introduce a sample into the gas burette, the sinter S.B. on the handling system was placed below the surface of the mercury covering the sinter on the calibration bulb. The air in sinter S.B. was then removed by raising it to touch the sinter S.A. and evacuating. Then the sinter on the gas bulb was pushed up to touch the other two and the required amount of gas allowed to enter the burette. Readings of the mercury levels in the burette were taken before and after introducing the gas, and the temperature of the laboratory, so that, since the volume of the tube from the sinter S.A. to the gas burette scale was known, the number of moles of gas injected could be calculated. The gas was expanded from the burette into the mixer, and from there into the five litre bulb and Metrosil leak area of the system.

The sample bulbs containing the gas to be analysed were attached to the handling system by a B.14 joint at D; this part


SOLENOID
STEEL ROD
ASBESTOS RING
TO 5 LITRE BULB
RUBBER RING
TO METROSIL LEAK

F I G U R E (20).

of the system up to the tap T_5 on the bulb was evacuated, cut-offs A and B being raised to isolate the leak, the pumps isolated by closing tap T_4, cut-off B lowered and the sample expanded into the five litre bulb. Cut-off A was then lowered and the sample allowed to diffuse through the Metrosil.

During preliminary experiments on the analysis of mixtures of hydrogen and methane, it was found necessary to wait for some time for the sample voltages to reach a steady value due to poor mixing of the gases, so the five litre bulb was altered to have an entrance and exit, each of which could be closed by a solenoid valve, S.V.1 and S.V.2, so that using the Toepler pump already in the system, the gases could be thoroughly mixed before any voltages were recorded. The second solenoid valve required was constructed similarly to that already in the system as in Fig.(20). The method of mixing the gases was to shut one valve, draw down the mercury in the mixer, then open the second valve and shut the first, and raise the mercury in the pump. Mixing was complete when the voltage settled to a steady value, and this usually required six complete operations of the mixer.

Description of the Mass Spectrometric Analysis of a Sample of Gas.

The electronics of the mass spectrometer were switched

on at least an hour before the instrument was required for an analysis, and the pumping changed over from the backing bulb to the rotary oil pump. When doing an analysis, in particular for hydrogen, it was not satisfactory to use only the mercury pump because the hydrogen back diffused into the tube and caused erroneously high readings.

The sample bulb was attached to the handling system at the joint (D), the air in the connecting tube pumped out, then the whole of the system evacuated to less than 10^{-5}mm.Hg. During this period, the background mass spectra were recorded, usually for peaks at m/e = 2^+, 15^+, 16^+ and 28^+, the trap current being maintained at a constant value. The system was then isolated from the pumps by closing taps T_3 and T_4, and the sample expanded into the rest of the apparatus, and the voltages for the products and the carrier gas recorded, keeping the trap current the same throughout. Usually it was necessary to use the low grid resistor to obtain the carrier gas voltage, as with the high grid resistor the voltage was beyond the linear range of the amplifier. The pressure of the sample was taken with the McLeod gauge. A known quantity of one of the calibration gases was then added to the sample as described previously, and the gases thoroughly mixed before the voltage was recorded. This calibration was repeated for each of the products for which an analysis was required, and

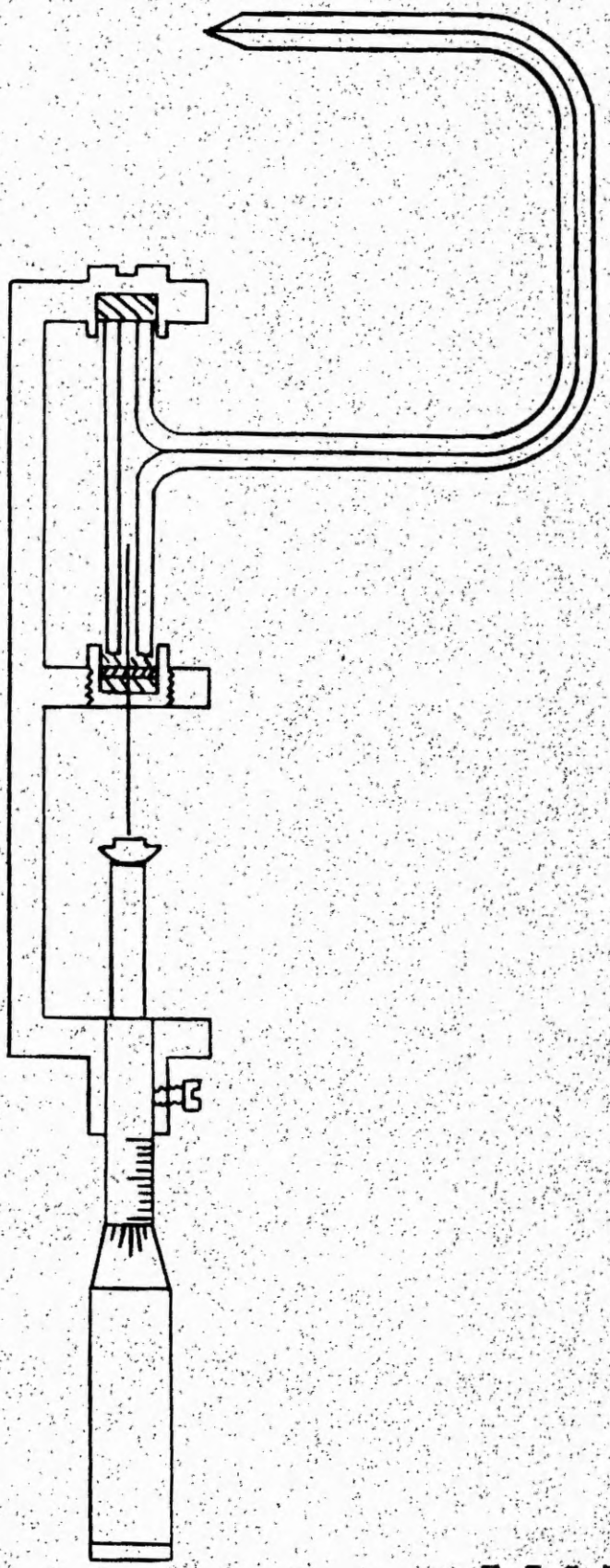


FIGURE (21).

then the system was evacuated in preparation for the next sample. Provided that the pressure and carrier gas voltage of each sample were recorded so that the sensitivity of the mass spectrometer could be found, it was not necessary to add calibration gases to each sample.

LIQUIDS.

Two methods of analysis were used:-

(1) The undecomposed toluene containing the small amount of the liquid products was weighed in the small sealed traps in which it was collected.

(2) To investigate the nature of the products, after weighing, a small quantity of the liquid was injected into the mass spectrometer through the mercury covered sinter S.D. on the gas handling system, Fig.(19), using a microburette.[11] This consisted of a mercury filled capillary tube attached to a micrometer gauge as shown in Fig.(21). Calibration samples of pure pre-pyrolysed toluene and a mixture of a known amount of benzene in toluene were also injected. The method of analysis was similar to that used for the gases, backgrounds in the regions m/e = 92^+, 91^+, 90^+, 79^+, 78^+, 77^+, being recorded, and then the voltages for the samples and calibration liquids.

A difficulty in the analysis of the liquids which was not experienced with the gases was that the trap current was markedly depressed as soon as the hydrocarbon entered the ionisation chamber. This was due to carbon being deposited on the filament and so lowering the emission. In order to counteract this effect the trap current was set to the lowest value consistent with stability during the background scans, so that there was as little difference as possible between its value for the background and sample scans.

SOLIDS.

The solid reactants and products were analysed by:-

(1) Ultra-violet Spectrophotometry, and

(2) Mass Spectrometry.

(1) A Unicam S.P. 500 photoelectric spectrophotometer was used. The solids analysed were those collected in the heated traps after runs on the pyrolysis of toluene, fluorene and both materials together.

To determine the amount of fluorene passed in an experiment, a standard spectrum of the pure substance was required. This was obtained by making up a solution of fluorene in methanol and recording the spectrum from 240 - 310 $m\mu$. A graph was plotted with log. (extinction coefficient), and the wave-length as variables.

The solid samples from the runs were prepared for analysis by dissolving them out of the heated traps with methanol, transferring the solutions to 200 ml. graduated flasks, and making the solutions up to the mark. These solutions were further diluted according to the quantity of material present to give an optical density of from 0.4 to 0.8, this being the range where the instrument is most accurate.

In the fluorene estimations the optical densities were recorded at 260 and 271 mμ, the calibration graph was used to obtain log.(extinction coefficient) at these wave-lengths, and the quantity of fluorene calculated from the Beer's law relationship:-

Concentration in moles per litre =

optical density/extinction coefficient x cell thickness.

In this work the cells used were 1 cm. thick.

In the case of the solids obtained from the pyrolysis of toluene, the spectrum over the range 230 - 320 mμ was recorded for various samples, qualitative estimations only being made in these cases.

A difficulty arose when analyses for small amounts of dibenzyl in the presence of relatively large quantities of fluorene were required. This problem arose in connection with the relative amounts of the products formed by the

reaction of hydrogen atoms with toluene. Fluorene has a large extinction coefficient and also absorbs over the whole of the absorption range of dibenzyl, so that it was not possible to use ultra-violet spectrophotometry for these analyses. Modifications to the existing handling system for solids on the mass spectrometer were made so that it could be used for the estimation of solid materials.

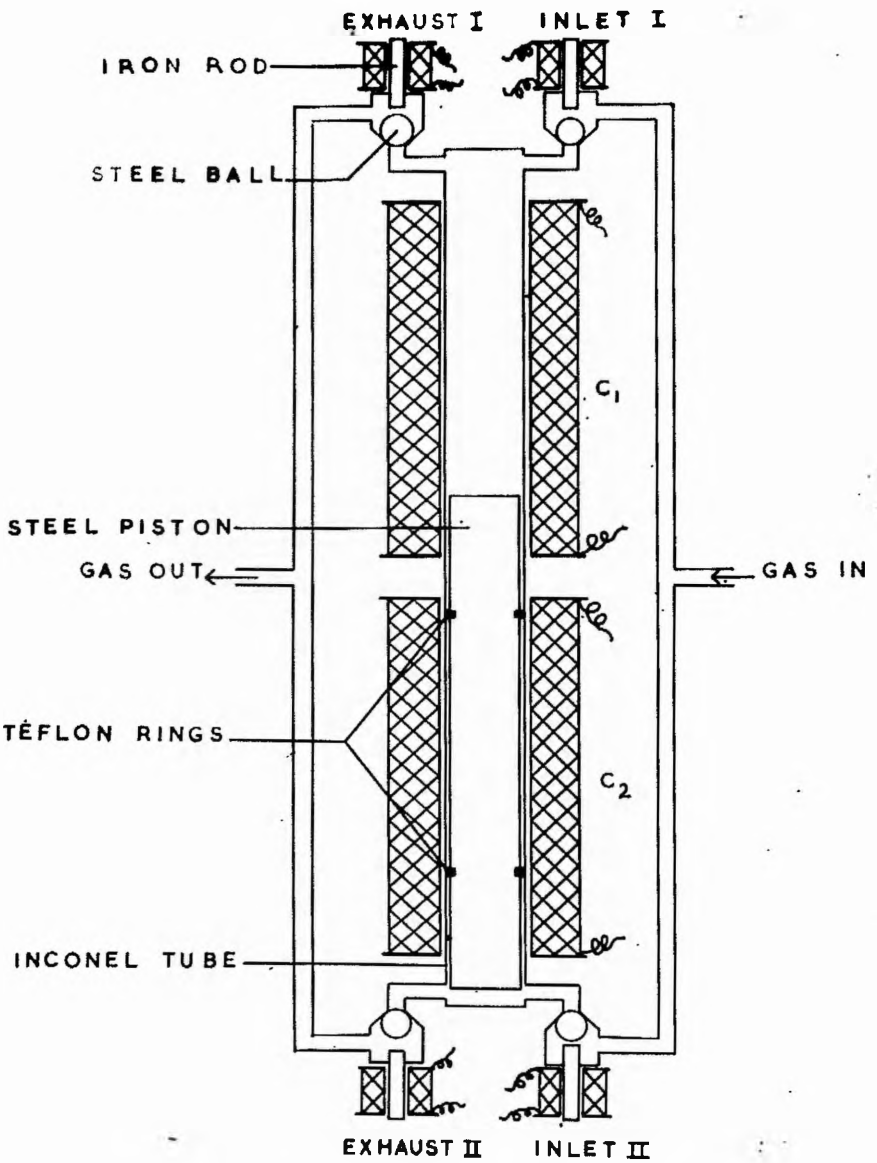
(2) Use of the Mass Spectrometer for the Analysis of Solids.

The existing handling system for the qualitative analysis of solids consisted of three metal valves in series, similar in construction to that shown in Fig.(11). These valves were used to isolate the injection reservoir, the inlet line to the mass spectrometer, and the vacuum lead from each other. A heated trap was connected in the vacuum lead, and was used to collect the materials after analysis. The inlet line to the mass spectrometer led to a Metrosil 4F porous plug leak placed by means of an internal seal in the centre of a two litre flask enclosed by a furnace; the temperature of the latter was controlled by a resistance thermometer controller, and measured using a chromel-alumel thermocouple. The glass lines connecting the injection valve and the ionisation chamber with the flask were heated to about 100°C.

This system was not found to be very satisfactory for quantitative work because, after injection, a considerable time

elapsed before the maximum peak height was reached: e.g., 5.3 mgm. dibenzyl was injected and the time taken for the peak m/e = 182^+ to reach its maximum was 24 minutes, the temperature of the glass lines being 80°C. It was found by injecting further quantities of dibenzyl, that the time required for the maximum peak height to be reached depended, to a large extent, on the temperature of these lines. With the lines at 200°C. the maximum peak height was reached in ten minutes, and with the existing apparatus it was not possible to improve on this value. To further reduce this time lag it was thought desirable to have the leak as close to the ionisation chamber as practicable, and also it was known that the samples should be mixed before passing through the leak, so that no errors should arise due to the preferential evaporation of one component of a mixture and the withdrawing of a non-uniform sample into the mass spectrometer.

To mix the samples it was necessary to pump the vapours round a circulation system which at some point contained a Metrosil leak. Since the whole of this part of the system had to be heated to 150 - 200°C., it was not possible to use a mercury vapour circulation pump, and a survey of known possibilities did not suggest a design which covered all requirements. In the first place, the pump had to work at pressures less than 5 mm.Hg., and this produced difficulties



CIRCULATION PUMP
(SCHEMATIC)

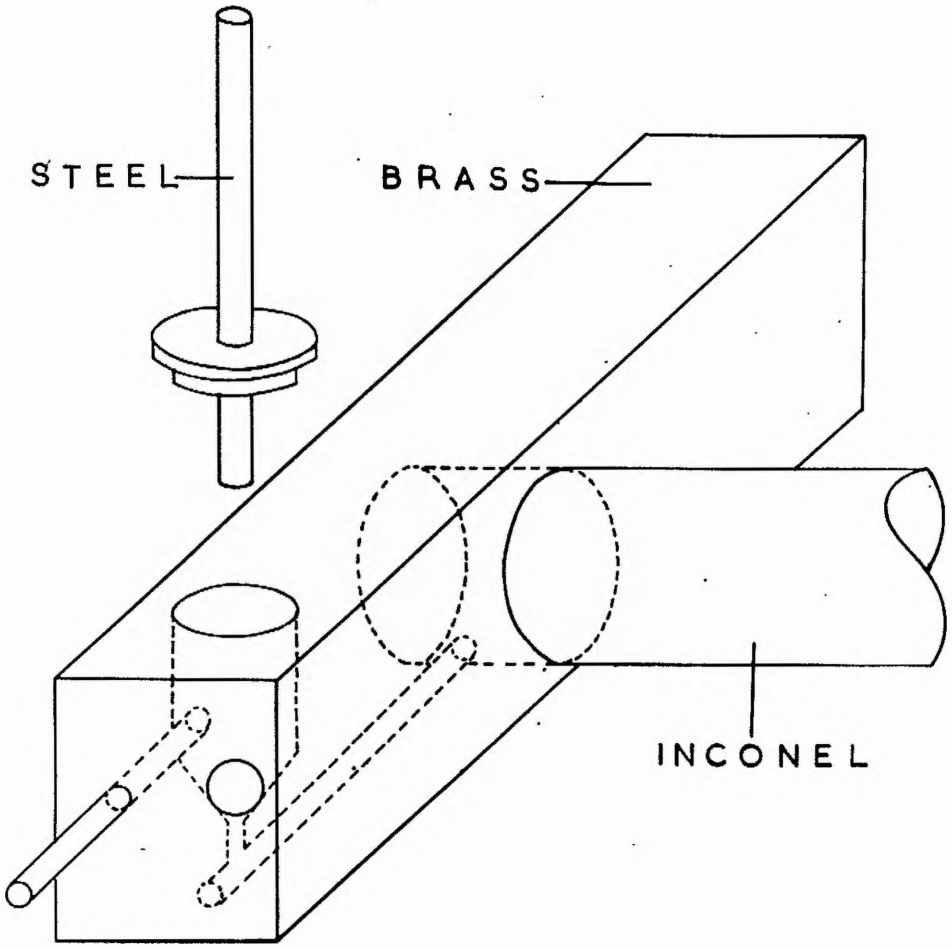
FIGURE (22).

with valves. Compression of vapours at this pressure cannot lift valves, so mechanical assistance had to be provided and synchronised with the movement of a diaphragm or piston.

Since the pump had to be vacuum tight, the use of rotating shafts through glands was turned down, and operation of the mechanism had to be by electromagnetic induction through a vacuum tight shell, or by the use of flexible bellows. Since the only seamless bellows available were in brass, and the life of these had been found to be low at elevated temperatures, this possibility was not pursued.

The first attempt made was to use a high speed fan driven by the reaction of a rotating electrical field and motor armature. The motor armature, fan and bearings were mounted inside a thin non-magnetic alloy case, and the stator slipped over this case. It was found that the efficiency of the fan fell off as the pressure was lowered, and at the working pressures required, it was of no value.

It was decided to construct a positive displacement type of pump, and that shown in Figs. (22) and (23) proved satisfactory. A light steel tube had two steel plugs silver soldered into each end, and was provided with two grooves into which piston rings of polytetrafluorethylene (Teflon or Fluon) were fitted. This piston was pulled to and fro in an inconel tube by the alternate activation of two coils fitted over



VALVE BLOCK FOR CIRCULATION PUMP

FIGURE (23).

the tube and co-axial with it. It was found to be important to allow about 0.003 inch between the piston rings and the wall when cold as the plastic expanded much more than the metal on heating.

The pump cylinder had a brass block at each end containing the valve system. This consisted of a ball bearing sitting in a conical seat and pulled upwards when required by the attraction of an electromagnetic armature. The brass blocks were heated by elements made from Nichrome tape wound on mica, and bolted to the blocks.

The electrical switching arrangements are shown in Fig.(24) and, in practice, involved two cam operated five amp micro-switches S_1 and S_2 worked from a common shaft rotating at 60 - 100 revolutions per minute, the number of revolutions being controlled by the variable resistance R.

This pump was included in the solids handling system as shown in Fig.(25), and at the same time, the position of the leak was changed to one immediately outside the ionisation chamber.

Satisfactory trials with the apparatus were made; various solid materials such as dibenzyl and diphenylmethane were injected and the time taken for the parent peak to reach its maximum value noted, e.g., 4.9mgm. dibenzyl was injected and the time taken for the peak m/e = 182^+ to reach its

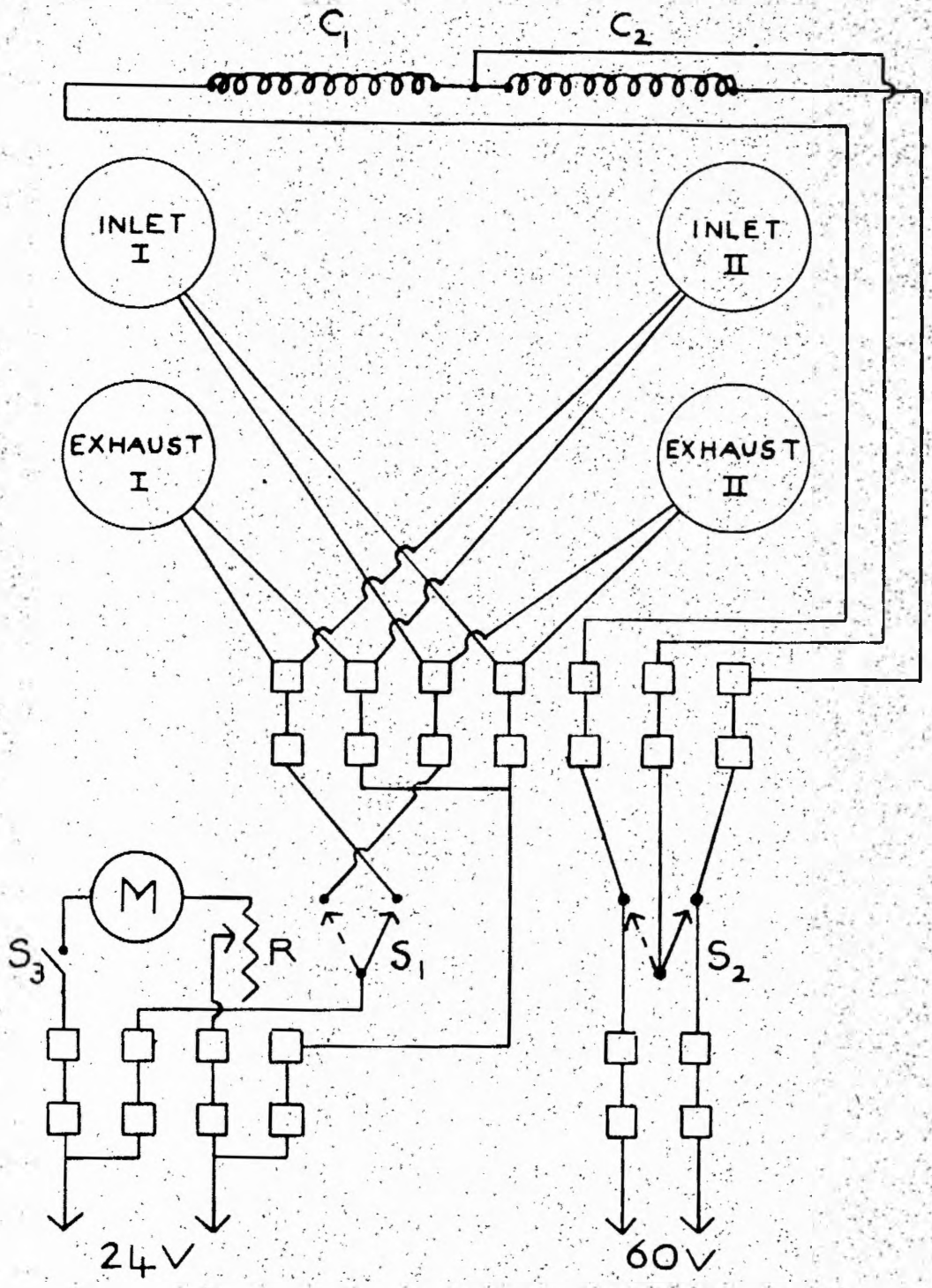


FIGURE (24).

maximum was four minutes, the temperature of the glass lines being 140°C.

The procedure for the analysis of solid materials was as follows; the mass spectrometer was prepared for use, and the circulation pump and all heaters in the handling system switched on, the furnace temperature being about 150°C. The samples for analysis were weighed into small ignition tubes on a Stanton semi-micro balance, the quantities used being of the order 5 mgm. or less, and the tube was placed in a glass reservoir sealed to a metal tube and flange which was bolted to the injection valve. The whole apparatus was evacuated to 10^{-5} mm.Hg. and background scans in the required mass region taken, then the sample was injected by surrounding the reservoir with a boiling water bath and opening the valves connecting it with the mass spectrometer. Scans of the sample were done as far as possible with a constant trap current, as it was again noted that this was lowered considerably after the injection of a hydrocarbon.

In order to have some record of the sensitivity of the instrument, a known pressure of nitrogen was injected through the gas handling system at the same time as the solid, and the height of the peak m/e = 28^+ was recorded. The mass spectra of the following pure materials were

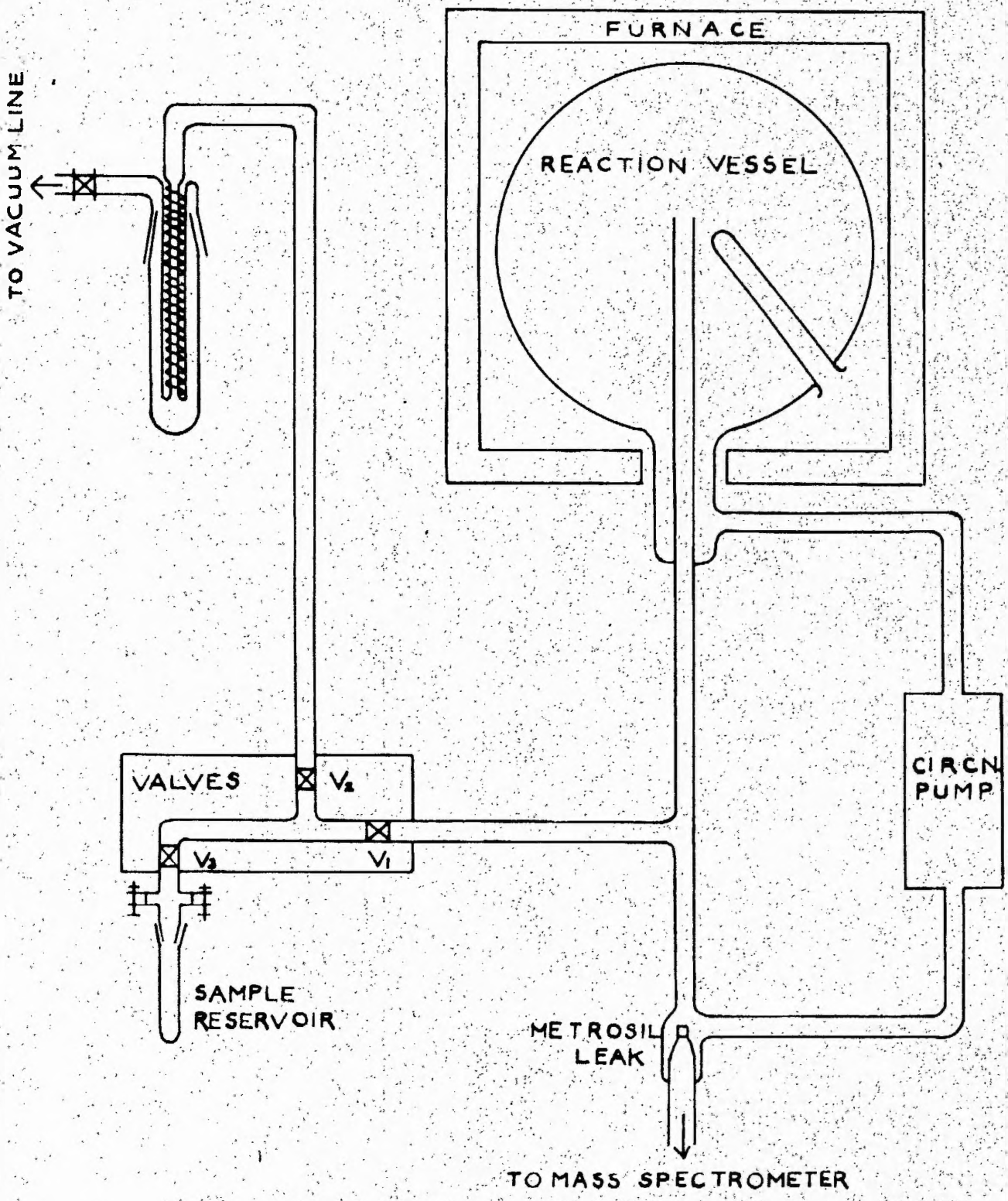

FURNACE
REACTION VESSEL
TO VACUUM LINE
VALVES
V_2
V_3
V_1
CIRCN. PUMP
SAMPLE RESERVOIR
METROSIL LEAK
TO MASS SPECTROMETER

FIGURE (25).

observed for use in calculating the qualitative and semi-quantitative composition of the solid products obtained:- dibenzyl, diphenyl, 4-methyldiphenyl, 4-4'-dimethyldiphenyl, stilbene, diphenylmethane and fluorene. (See Appendix II).

GENERAL PROCEDURE FOR RUNS.

The current for the furnace heater was switched on, and evacuation of the whole apparatus was started several hours before the start of an experiment. The heaters for the injection valve, glass lines and copper oxide furnace were also switched on so that the apparatus was evacuated hot. The reactants were then degassed, in the case of toluene by freezing the liquid and opening the valve to the vacuum line to evacuate the reservoir, closing the valve and melting the toluene; the cycle of operations was repeated three times.

The Wood's metal bath was melted, raised round the boiler of the circulation pump, and its temperature set for the pressure of carrier gas to be used that day. Liquid air baths were placed round traps $T.R._1$ and $T.R._2$. (See Fig.3).

At least an hour before commencement of the run, the constant temperature baths for the injection reservoirs were heated, the heated collection traps surrounded by liquid air baths, and the thermal conductivity gauge connected to the batteries and its surrounding cold water bath filled.

For an experiment on the pyrolysis of toluene alone,

the procedure was then as follows:-

The vacuum and flow sides of the valve and tap T_{12} connecting it with the vacuum line were closed, the liquid air bath round the toluene reservoir replaced by the pre-heated water bath, and the flow system isolated from the rest of the apparatus by closing taps T_1 and T_2. The manostat was filled with the carrier gas, and the required number of fillings injected into the system via tap T_5. Taps T_{13} and T_{14} were closed so that the products did not flow over the copper oxide, and the second and third of the three parallel series of collection traps isolated from the flow line.

The rate of flow of the carrier gas was adjusted to the desired value, and the McLeod gauges left run up to eliminate fluctuations in the gas pressure which had an adverse effect on the steadiness of the conductivity gauge reading. All cold baths were filled up; the bridge of the thermal conductivity gauge balanced, and tap T_9 closed to prevent hydrogen entering the compensating bulb. After about fifteen minutes, when it was certain that this point of balance was stable, the furnace temperature was read and the injection valve opened, the time being noted. Galvanometer readings were taken every minute, and McLeod readings in between the galvanometer readings, the number of these

depending on the length of the run, minute readings not being necessary. The length of the run depended on the amount of hydrogen made, and was never allowed to be so long that it was necessary to change to a less sensitive range of the galvanometer. When a suitable amount of hydrogen had been made, the valve was closed, the time being noted, the furnace temperature read again and the hydrogen either burned out by allowing the gas to flow over the heated copper oxide, or tap T_{16} was closed and the gas pumped into the sample bulb via the Toepler pump. In the former case, a second run was possible as soon as the combustion of the hydrogen was complete and, in general, a series of from six to fifteen runs was made, the number depending on the quantity of toluene passed. At the end of the series, known quantities of hydrogen were injected from the gas burette for calibration purposes, and the galvanometer readings noted. The apparatus was then evacuated, and the toluene and liquid products distilled into the B.10 traps as described on page 53. All heaters were then switched off, the batteries disconnected from the thermal conductivity gauge, air let into the apparatus, and the traps containing the liquid and solid products withdrawn for the analysis of their contents.

In the latter case, when the gases were to be analysed on the mass spectrometer, after removal of the carrier gas and gaseous products the gas sample bulb was removed and replaced, the new bulb evacuated, and the run repeated. A hydrogen calibration was made in one of the experiments, and the liquid and solid products dealt with as before.

For experiments using fluorene only, the procedure was similar except that it was necessary to heat the injection valve to a higher temperature, and no liquid products were formed.

For experiments with toluene and fluorene, it was necessary first to perform blank runs on the reactants separately as above, and then to do a combined run, the experiments being made in the following sequence:-

(1) Runs with fluorene alone until the surface of the reaction vessel was conditioned, a hydrogen calibration being made in the last of these experiments.

(2) At least two runs using toluene alone to ensure that the surface was also properly conditioned for toluene.

(3) Complete evacuation of the apparatus followed by a blank toluene run in which the gaseous products were collected for mass spectrometric analysis.

(4) The injection of more nitrogen followed by a combined toluene - fluorene run. When the apparatus was

ready for use, the toluene injection valve was opened and, after one minute, the fluorene valve. Galvanometer and McLeod readings were taken as before, and the fluorene valve closed one minute before the toluene valve. The gases were collected in a sample bulb and analysed on the mass spectrometer.

Details of the calculation of velocity constants, etc., from the experimental data are given in Appendix I.

TABLE V

Temperature 772°C.

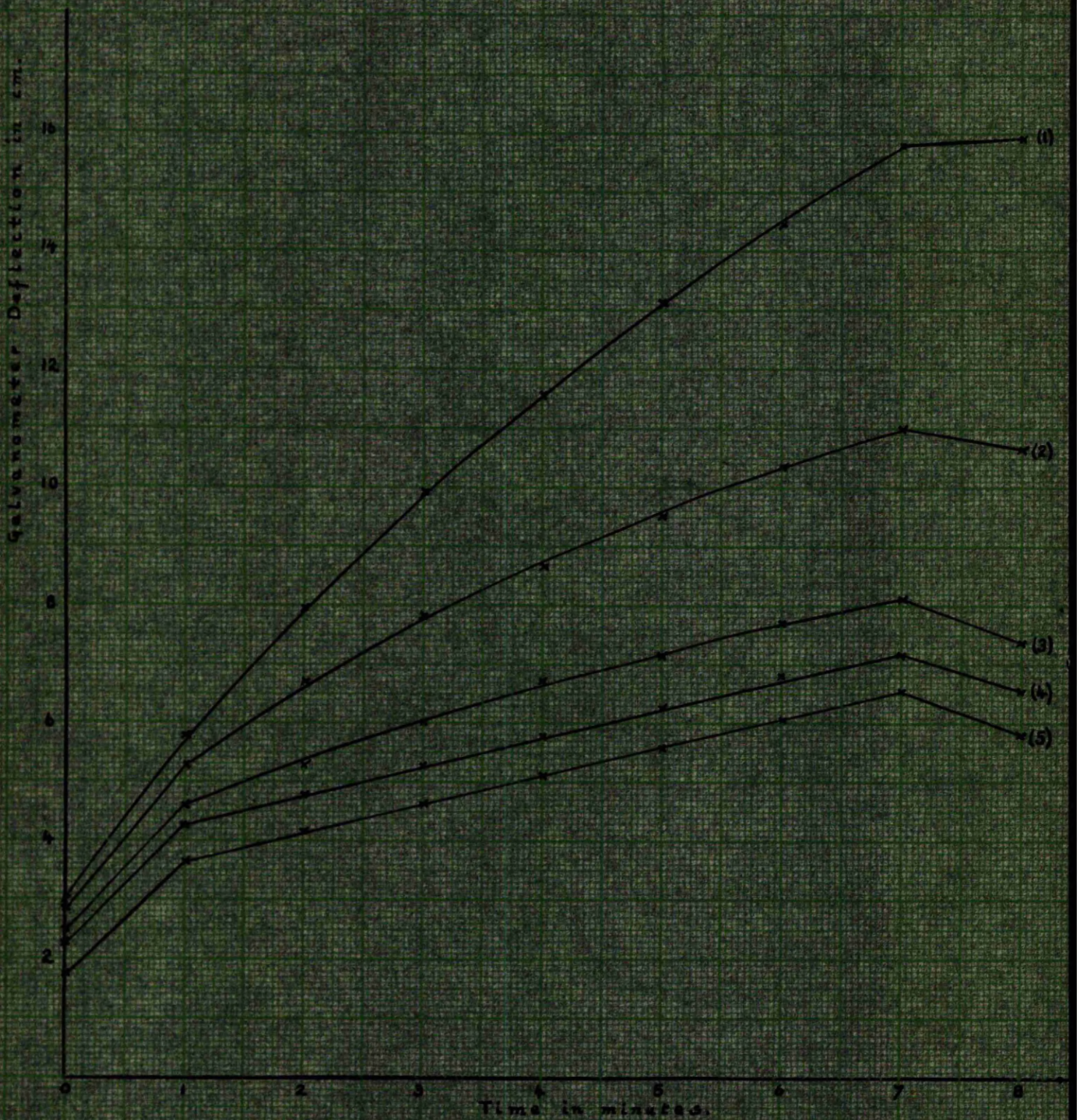
Time of Contact 1.02± 0.15 seconds.

Run 25.5.55.	% Decomposition.	Run 27.5.55.	% Decomposition.
1	8.56	1	9.01
2	10.32	2	11.46
3	12.22	3	13.12
4	9.73	4	10.68
5	7.88	5	8.67
6	7.91	6	8.15

RESULTS OF EXPERIMENTAL WORK.

As a preliminary to work on toluene, some experiments on the fluorene pyrolysis were undertaken to verify that McCrae's rate of decomposition could be reproduced in the apparatus which had been constructed. The preliminary experiments showed a production of gas which was greatly in excess of the calculated amount for the temperature, time of contact and concentration of fluorene used. Moreover, the percentage decomposition decreased in a series of runs, and seemed to settle down after about forty minutes operation, as shown by the data in Table V. Initially the rate of reaction was determined by withdrawing the carrier gas and analysing for hydrogen - a process which was slow and made changes in the rate of production rather difficult to observe.

It was obvious that a continuous record of hydrogen production would be more suitable, and the thermal conductivity gauge described on page 61 was installed for this purpose. This was a great improvement, and the rate of change of the out of balance galvanometer reading gave a rapid record of the progress of the reaction. It was proved by direct additions of hydrogen from the gas burette to the


Galvanometer Deflection in cm.
16
14
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
Time in minutes.
(1)
(2)
(3)
(4)
(5)

F I G U R E (26).

circulation system that the out of balance bridge reading bore a linear relationship to the additions up to magnitudes of the latter much higher than the production of hydrogen in experiments. The type of record is illustrated in Fig.(26) from a run on the pyrolysis of toluene. The initial and final discontinuities on each graph were due to the minor pressure changes resulting from the opening and closing of the injection valve. The sequence of graphs (1) to (5) Fig.(26) shows, however, a decay of rate of decomposition to a steady value, which was a typical finding, and suggests a progressive seasoning of the reaction vessel. This behaviour was shown by both fluorene and toluene, and it was found that a pre-treatment with fluorene left the vessel in a condition where the pyrolysis of toluene reached a steady state after only one run. On one occasion, an exploratory experiment on diphenylamine was conducted for another worker, and this was followed by pyrolysing toluene. The initial rate of decomposition of the toluene was twelve times faster than the final steady state reached. Thus pre-treatments with some compounds can have the opposite effect to that noted with fluorene.

The usual reason advanced for similar behaviour in other systems is the deposition of a layer of carbon on the wall. Consequently, after several runs with toluene, the

furnace was allowed to cool out of contact with air, (to avoid combustion of any carbon), and the tube removed for examination. There was no observable carbon layer. However, later experiments in a static reaction system attached to a mass spectrometer did show a thin carbon layer, which could also be detected by the generation of a quantity of carbon dioxide after the admission of oxygen.

TABLE VI

Sample.	A	B
14	69.8% H_2, 30.2% CH_4	67.5% H_2, 32.5% CH_4
21	81.2% H_2, 18.8% CH_4	82.4% H_2, 17.6% CH_4
13	58.6% H_2, 41.4% CH_4	68.2% H_2, 31.8% CH_4
4	72.5% H_2, 27.5% CH_4	59.2% H_2, 40.8% CH_4

THE GASEOUS PRODUCTS.

POINTS ON MASS SPECTROMETRIC ANALYSES.

(a) Hydrogen Analyses.

The work on pre-treatment of the reaction vessel had resulted in the continuous observation of hydrogen formation by the thermal conductivity gauge system, and this provided a second method of analysis with its own standardisation procedure based on the gas burette injections into the circulation system.

It was found that the analyses for hydrogen by the thermal conductivity gauge and the mass spectrometer, while in agreement for some samples showed marked disagreement for others. This is shown in Table VI where column A gives the percentage hydrogen and methane when both were determined by mass spectrometer, and column B gives values for hydrogen determined by the thermal conductivity gauge and uses the same mass spectrometer value for the gram moles of methane.

Since the cause of this was not readily ascertained, a series of blank experiments was undertaken which was designed to check the entire mass spectrometer procedure for analysis.

This involved the following stages:-

(1) Three mixtures of hydrogen and nitrogen were prepared in the circulation system by injecting hydrogen from the attached gas burette into nitrogen in the system. The proportions used were such as could be formed in a pyrolysis run, and after the mixtures were made they were extracted into sample bulbs by the Toepler pump as described on page 54.

(2) The samples were fed separately into the mass spectrometer and the voltages associated with m/e = 2^+ and 28^+ were measured, together with the total pressures of the samples.

(3) The samples were removed by evacuation of the handling system and various pressures of hydrogen substituted. The voltages for m/e = 2^+ were measured in order to provide data for a calibration graph for the instrument of pressure (i.e., gram moles in system) of hydrogen against measured voltages.

By comparing the values for m/e = 2^+ in (2) with the calibration in (3), the following were obtained:-

TABLE VII

	(i)	(ii)	(iii)
Actual moles H_2 injected x 10^5	0.64	1.18	2.58
Analysed moles H_2 injected x 10^5	0.90	1.44	4.09
(Actual H_2/ Analysed H_2) x 100	71%	82%	63%

The percentage errors were clearly not the same and the data in (2) were re-examined. The voltages at m/e = 28^+ divided by the measured pressure of gas feeding the mass spectrometer (which was almost entirely that of the nitrogen) gave sensitivity to nitrogen figures (S_{N_2}) of 6.43, 6.18, 7.92 volts/mm. Thus the instrument's sensitivity was altering seriously between the admission of the samples. The time covering the handling of three samples through stage (2) was about one and a half hours. While the reason for the sensitivity change was not clear it seemed reasonable to suppose that more consistent values of "analysed moles of hydrogen x 10^5" would be achieved if the measured voltages were corrected to allow for this change. Therefore, selecting 6.18 volts/mm. as the arbitary standard, we obtain an analysis figure for:-

(i) of 0.90 x 6.18/6.43 = 0.87, and for

(iii) 4.09 x 6.18/7.92 = 3.2.

Thus table VII is modified to :-

TABLE VIII.

	(i)	(ii)	(iii)
Actual gram moles H_2 x 10^5	0.64	1.18	2.58
Analysed gram moles H_2 x 10^5 corrected to S_{N_2} 6.18 volts/mm.	0.87	1.44	3.2
(Actual H_2 /Analysed H_2) x 100	74%	82%	81%

This adjustment is based on the idea which is common in mass spectrometry that the relative sensitivity of hydrogen and nitrogen (S_{H_2}/S_{N_2}) remains constant.

The corrected analysis figures when plotted against the actual gram moles of gas injected, give a much more linear relationship than the data of Table VII. However, the considerable discrepancy of the absolute values suggests that the arbitarily chosen value of sensitivity to nitrogen was, in fact, incorrect for this purpose. There is, of course, no guide when making a choice of a common instrumental sensitivity to which the readings can be reduced; the data of Table VIII merely point out that the measurements done on a series of samples can be rendered more comparable by this reduction to a common sensitivity to nitrogen.

The remaining discrepancy in absolute quantities noted in Table VIII could be eliminated if the sensitivity of the instrument to nitrogen was known at the instant of the calibration with hydrogen in stage (3). Clearly this was not possible if pure hydrogen was used for calibration and, since the sensitivities changed rapidly, it seemed that the calibrating gas could, with advantage, be a mixture of hydrogen and nitrogen.

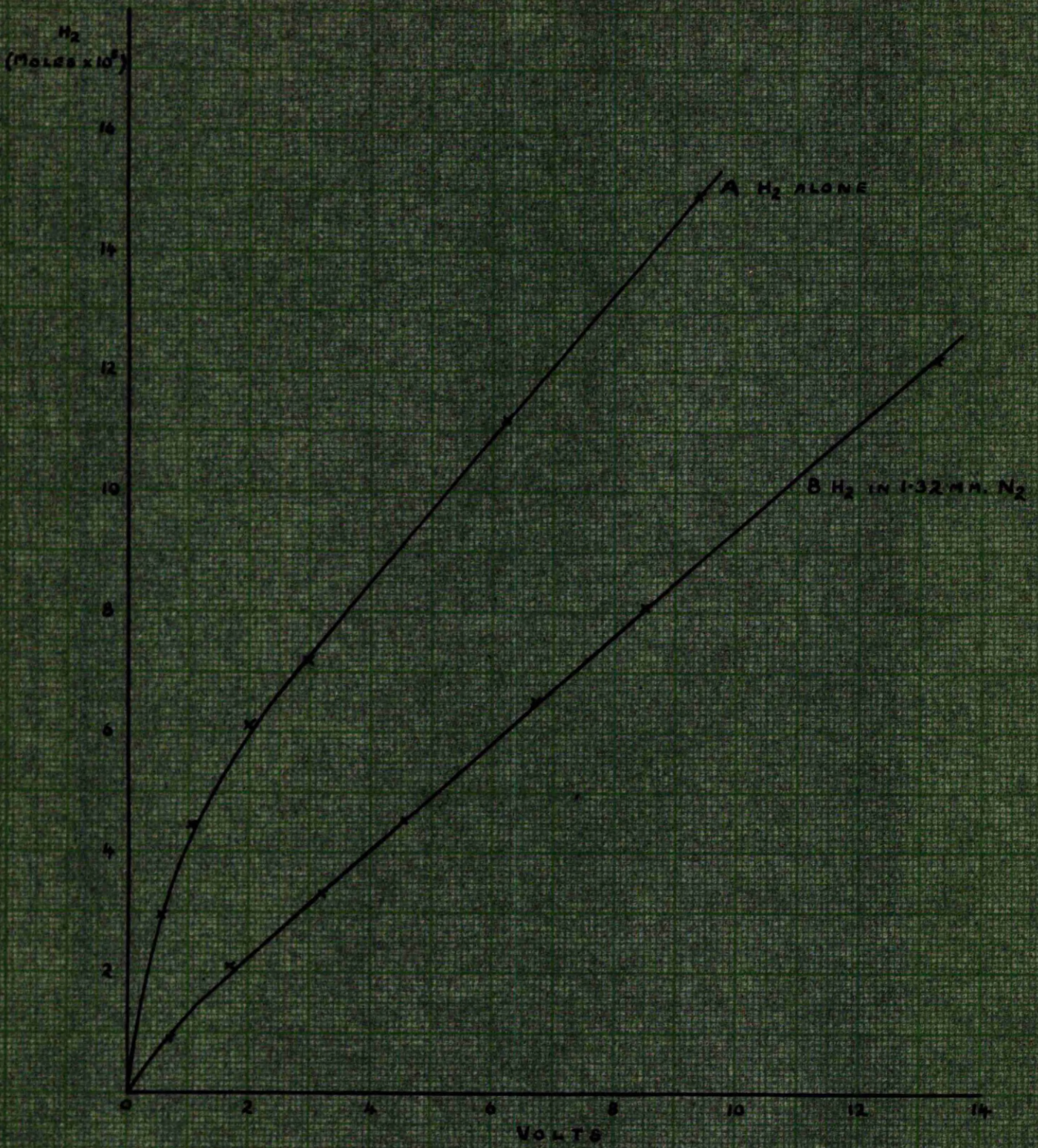

H_2
(Moles x 10^8)
16
14
12
10
8
6
4
2
0
2
4
6
8
10
12
14
Volts
A H_2 alone
B H_2 in 1·32 mm. N_2

FIGURE (27).

Before implementing this finding, another fact was observed which emphasised the need for the change contemplated. Two calibrations of the mass spectrometer were done. In the first, pure hydrogen was admitted in increasing amounts to the evacuated handling system, while, in the second, the same range of hydrogen additions was made to the system when filled with 1.3 mm. nitrogen. The data are shown in Fig.(27), and when using pure hydrogen - graph A, there was a marked non-linearity over the range of investigation. In some earlier calibrations with pure hydrogen, the data had tended to be restricted to the portion of the graph near the origin where a reasonably linear region of lower sensitivity existed. This was in order to produce calibration voltages of the size of the sample voltages usually encountered. A comparison of the two curves in Fig.(27), however, shows that a serious error could result from this practice. Calibrations of the type resulting in graph A were not suitable for assessing the hydrogen content in samples with excess nitrogen, which were more appropriately treated by graph B.

This departure from linearity in calibrations was troublesome, and some attempts were made to discover its origin. The general process of mass spectrometry involves the admission of gas through a porous plug or fine hole, and

ionisation of it within the instrument. It was thought that the cause could be either:-

(a) Some peculiarity in conditions of gaseous flow through the particular porous plug in use, or

(b) Peculiarities due to the type of porous plug used, or

(c) Conditions in the ionisation region of the mass spectrometer.

It was found that nitrogen calibrations showed the same effect at low pressures, and that the type of results obtained did not depend on which of three porous plugs of different porosities were used to admit the gas. These points suggested that the cause lay in the behaviour of the ionisation chamber of the mass spectrometer. In order to characterise the flow conditions more closely, the rate of pumping gas through the porous plug was determined for two separate initial pressures, one chosen in the higher concentration range of graph A, and the other in the lower part of the graph. Within the accuracy of the experiments the rate of pumping gas through was proportional to the initial pressures. This points to conditions within the ionisation box as the cause of the behaviour. Since non-linear calibration curves were not always obtained, and since it is known that the state of cleanliness of the ion

gun can result in differences in efficiency, the site of the troubles noted appeared to be located - if not explained.

As far as practical analyses were concerned, the lessons drawn from the findings were to speed up the process of calibration by injecting the standardising gas into the sample as soon as the measurements on the latter had been made. In all work of this thesis the analyses were conducted in the presence of a large excess of carrier gas, and this could conveniently form the reference standard for sensitivity changes. Adequate mixing of all calibration additions was found to be essential and the arrangements for this have been described and illustrated (page 86 and Fig.19).

As a result of applying these findings a much greater degree of agreement between the mass spectrometric and thermal conductivity analyses was possible.

(b) Evaluation of Amounts of Hydrogen from Data.

The background and sample voltages for the peak at m/e = 2^+ were taken together with the voltages at m/e = 28^+ or m/e = 14^+ and the total pressure in the handling system. A hydrogen calibration was obtained by injecting a known quantity of hydrogen into any sample whose nitrogen sensitivity was known, and that was analysed on the same day. The hydrogen made was calculated as follows:-

Mass spectrometer voltages at m/e = 2^+.

Background = 0.014 volts

Background + sample = 0.313 volts

Sample = 0.299 volts

Nitrogen sensitivity = 0.628 volts / mm.

Hydrogen calibration.

Nitrogen sensitivity = 0.676 volts / mm.

Pressure of gas injected = 2.85 cm. at 299.4°K.

Volume of gas injected = 0.0294 litres.

Therefore gram moles of hydrogen injected

$$= \frac{2.85 \times 0.0294}{76 \times 0.082 \times 299.4}$$

$$= 4.49 \times 10^{-5}$$

This quantity of hydrogen gave an increase equal to 0.3785 volts of the peak m/e = 2^+ over the background value. At a nitrogen sensitivity of 0.628 volts / mm. this voltage

$$= 0.3785 \times 0.628 / 0.676$$

$$= 0.3517 \text{ volts.}$$

From the calibration:-

0.3517 volts were given by 4.49×10^{-5} gram moles of hydrogen.

Therefore 0.299 volts were given by

$$4.49 \times 10^{-5} \times 0.299 / 0.3517$$

$$= \underline{3.817 \times 10^{-5} \text{ gram moles hydrogen.}}$$

But the volume of gas analysed by the mass spectrometer was a certain fraction of the gas collected, this fraction being dependent on the volume of the sample bulb, (see page 54 for values of this fraction). In this case the ratio of the total volume of the collecting system to the volume of the sample bulb was 1.48 : 1.

Therefore, the total amount of hydrogen made in the experiment = $3.817 \times 10^{-5} \times 1.48$ gram moles

= $\underline{5.65 \times 10^{-5} \text{ gram moles.}}$

(c) Analysis of Methane.

The standard mass spectrum of methane was obtained by injecting the pure sample from the Chemical Research Laboratory, Teddington, into the mass spectrometer, and then calculating the intensities of the peaks at m/e = 15^+, 14^+, 13^+, 12^+, relative to the intensity of the peak m/e = 16^+. These compared reasonably with the data supplied by the American Petroleum Institute, see Appendix (II), considering that this type of data is peculiar to the machine on which it is obtained and its operating conditions.

For purposes of analysis, the peaks at m/e = 12^+ and 13^+ were too small to yield accurate results; nitrogen in the form of the ion N_2^{++} contributes to the peak at m/e = 14^+, and since the amount of nitrogen injected varied with each sample,

this would provide an unknown background to the contribution from methane. Objections to the use of the peak at m/e = 15^+ are similar, an ion of mass 15 is found in small quantities in the mass spectrum of most hydrocarbons, for example, ethane and toluene. It was decided to calculate the amount of methane formed from the height of the peak at m/e = 16^+, but also to record the height of the peak m/e = 15^+ as a check on the former value; analyses where the ratio m/e = $15^+/16^+$ was appreciably different from 0.85 being repeated when possible or discarded.

The method for calculating the amount of methane formed from the experimental data was exactly similar to that for calculating the amount of hydrogen made.

(d) C_2 Hydrocarbons.

These were the only other hydrocarbons observed in the mass spectra. For analytical purposes the peaks of interest are m/e = 26^+ to m/e = 30^+. Both ethane and ethylene have their strongest peak at m/e = 28^+, but this was useless since it is also given by the nitrogen carrier gas present in considerable excess. The isotopic contribution from nitrogen to m/e = 29^+ was another undesirable feature, and in analyses for ethane, the peak at m/e = 30^+ was considered to be the most valuable.

While the ethane content could be derived with reasonable accuracy, the problem of determining the ethylene was much more difficult. In order to simplify the mass spectra, it was decided to use helium as a carrier gas. In theory this provides a complete solution, but the helium available unfortunately contained an appreciable quantity of nitrogen. The analyses have been based, therefore, on the solution of the following simultaneous equations applied to the voltages for peaks at 30, 29 and 28 mass numbers.

If we let x be the contribution in volts of ethane to the measured voltage at $m/e = 30^+$, and y and z respectively, the contributions of ethylene and nitrogen to the voltage for $m/e = 28^+$, then by using the cracking pattern data for ethane and ethylene (Appendix II), and the ratio $(N_2)^{29} / (N_2)^{28} = 1/133$, the following equations can be written:-

Volts measured at $m/e = 30^+ = x$

Volts measured at $m/e = 29^+ = 0.788\ x + 0.022\ y + 0.0075\ z$

Volts measured at $m/e = 28^+ = 3.51\ x + y + z$.

Solution of these equations gave values for the contributions of each substance to the peak heights, and by use of sensitivity data and the sample volume data, the gram moles of material could be deduced as previously shown for hydrogen.

Alternative methods of analysis consisted in determining the value of z by examining the helium carrier gas in a separate experiment, while a further line of approach was to use the peak heights for mass units 27 and 26. Both ethane and ethylene contribute to these, and a correction was necessary for the carrier gas due to impurity.

In spite of these efforts, we consider the ethylene data obtained as liable to considerable error arising from the various procedures outlined. If a more accurate estimation had been required, a pure inert carrier gas, with a molecular weight not in the 26 - 30 mass number region, would have been desirable. This was not available at the time and this aspect of the problem was not pursued.

TABLE IX

Date.	Hydrogen by Mass Spectrometer. % H_2 : % CH_4	Hydrogen by Thermal Conductivity Gauge. % H_2 : % CH_4	°C.
14.3.56	80.2 : 19.8	79.3 : 20.7	761
14.3.56	84.6 : 15.4	85.6 : 14.4	761
17.3.56	70.8 : 29.2	73.0 : 27.0	758
17.3.56	83.4 : 16.6	82.6 : 17.4	758
17.3.56	76.8 : 23.2	76.2 : 23.8	758
19.3.56	82.7 : 17.3	82.7 : 17.3	757
19.3.56	76.5 : 23.5	79.5 : 20.5	757
20.3.56	73.8 : 26.2	74.7 : 25.3	743
20.3.56	81.4 : 18.6	78.0 : 22.0	743
20.3.56	80.8 : 19.2	83.6 : 16.4	743
11.5.56	65.2 : 34.8	75.3 : 24.7	771.5
11.5.56	75.6 : 24.2	80.2 : 19.8	771.5
14.5.56	77.8 : 22.2	75.5 : 24.5	772
14.5.56	79.8 : 20.2	75.5 : 24.5	772
30.7.56	74.8 : 25.2	77.1 : 22.9	854
30.7.56	71.3 : 28.7	77.7 : 22.3	854
2.8.56	78.4 : 21.6	78.4 : 21.6	856
13.8.56	79.1 : 20.9	76.3 : 23.7	832
14.8.56	77.7 : 22.3	78.7 : 21.3	831
29.8.56	67.2 : 32.8	69.1 : 30.9	796
4.9.56	68.6 : 31.4	68.2 : 31.8	799
6.9.56	72.3 : 27.7	75.6 : 24.4	800
13.9.56	72.3 : 27.7	74.3 : 25.7	800
14.9.56	70.8 : 29.2	70.7 : 29.3	800

RESULTS.

Hydrogen and Methane.

An attempt was made to study the proportions of these substances formed over the temperature range 743°C. - 856°C., using contact times 0.75 to 1.08 seconds, and partial pressures of toluene of 0.60 to 1.84 mm. The hydrogen analyses were obtained from the mass spectrometer and the thermal conductivity gauge system, while the methane was analysed by the mass spectrometer only. The details are given in Table IX.

The average percentage hydrogen for those experiments where the two methods of hydrogen analysis did not differ by more than 3%, (18 out of 24), was 76.72. If the criterion is narrowed to experiments with the values within 1% of each other (10 out of 24), the value becomes 77.71. An examination of the data shows no significant variation with temperature.

C_2 Hydrocarbons.

The relevant analytical data are given in Table X. The ethane formed was less than 2% of the total (H_2 + CH_4). The relatively high figure for the ethylene may be due to the difficulties described earlier and would require further work to establish firmly.

TABLE X.

Date and Run.	15.9.56.	17.9.56 (2)	17.9.56 (3)
Temperature ^{o}C.	799	829	829
Carrier Gas	N_2	He	He
Time of Run (minutes)	20	10	10
Time of Contact (seconds)	0.804	1.107	0.935
Toluene (moles x 10^3)	7.08	3.823	3.705
Hydrogen (moles x 10^5)	0.995	6.49	6.55
Methane (moles x 10^5)	0.585	3.67	3.11
Ethane (moles x 10^5)	0.332	0.195	0.167
Ethylene (moles x 10^5)	No Analysis	4.11	1.74

RESULTS WITH DEUTERIUM AS A CARRIER GAS.

The idea behind these experiments was discussed earlier (page 44), and the first runs were conducted in an exploratory fashion to obtain a general picture of the reactions under these conditions.

Beginning with two toluene pyrolyses at 1120°K with contact times of 0.515 and 0.531 seconds, and toluene partial pressures of 1.44 and 1.48 mm., it was found that the carrier gas contained an average of 2.4×10^{-4} gram moles of hydrogen in the form of H_2 and HD. Since only 0.54×10^{-4} gram moles of hydrogen were anticipated on the basis of similar experiments in nitrogen as a carrier gas, it was apparent that the hydrogen production was 340% greater than expected. This raised a suspicion that exchange reactions on an unexpected scale might be operative and the organic materials would be substantially deuterated. The toluene was examined first, and whereas the relative intensities in its mass spectrum before pyrolysis were:-

$$91^+ = 100, \quad 92^+ = 74, \quad 93^+ = 5.5,$$

the values afterwards were :-

$$91^+ = 100, \quad 92^+ = 80.8, \quad 93^+ = 13.3.$$

This showed that the reactant was undergoing deuteration, and since there was no 94^+ peak, that the deuteration only proceeded as far as C_7H_7D and not to $C_7H_6D_2$.

The methane when examined gave the following relative intensity data:-

Peak	18^+	17^+	16^+
Normal CH_4	-	1.11	100
CH_4 from experiment with D_2 carrier gas	-	71.5	100

This again showed mono-deuteration which was anticipated from its mode of formation.

In the case of the C_2 hydrocarbons, the mass spectrum included a 31^+ peak which was 36% of the height of the 30^+ peak. This indicated the presence of C_2H_5D but the production of C_2H_3D could not be deduced so readily from a qualitative examination of the mass spectrum.

Turning to a more quantitative analysis of these observations, we deal first with toluene. In the analysis by Rylander, Meyerson and Grubb[33] of the mass spectra of deuterated toluenes, it can be observed that the relative intensity pattern for $C_6H_5CH_3$ was $91^+ = 148$, $92^+ = 100$, and that the sum of the relative intensities of the various

types of tropylium ion approximated to 148% of the parent molecular ion for their deutero compounds. In the St.Andrews' mass spectrometer the $91^+/92^+$ ratio was 139/100 and it seems reasonable to adjust their cracking pattern for $C_6H_5CH_2D$ proportionally to give this sum for our analyses. As a result, a spectrum is obtained for $C_6H_5CH_2D$ with the intensity pattern $91^+ = 15.9$, $92^+ = 119.5$, $93^+ = 100$, which can be rescaled for calculations as $91^+ = 13.3$, $92^+ = 100$, $93^+ = 119.5$. If the cracking pattern for $C_6H_5CH_3$ above is also rescaled in this way as $91^+ = 139$, $92^+ = 100$, $93^+ = 7.65$, and letting x volts be the contribution to the 92^+ peak due to C_7H_8, and y volts the contribution to the 93^+ peak due to C_7H_7D, the following equations can be derived relating these contributions to the observed volts for the peaks $m/e = 92^+$ and 93^+:-

Volts measured at $m/e = 93^+ = y + 0.0765\,x$

Volts measured at $m/e = 92^+ = 1.195\,y + x.$

By inserting $V_{93^+} = 0.17$ and 0.068 volts, and $V_{92^+} = 1.035$ and 0.433 volts for the runs at 1120°K, and $V_{93^+} = 0.063$ volts and $V_{92^+} = 0.536$ volts at 1073°K, equations which lead to the evaluation of x and y are obtained, and permit the calculation of $(y/x + y)100$ - the percentage of C_7H_7D. The percentages prove to be 9.82% and 9.05%, giving an average of 9.44 % at 1120°K, and 4.53% at 1073°K.

From the percentage deuterium in the final toluene we can calculate the amount of hydrogen ejected by exchange processes and likely to appear in the gas as $(5 \times 10^{-3} \times 9.4/100) = 4.70 \times 10^{-4}$ gram atoms, in the experiment at 1120°K. This gives 2.35×10^{-4} gram moles hydrogen exchanged for deuterium and represents rather more than the $(2.4 - 0.54) \times 10^{-4}$ gram moles 'extra' hydrogen found in the gas phase. For the experiment at 1073°K. the ejected hydrogen was 1.05×10^{-4} gram moles, while the 'extra' hydrogen found was $(0.998 - 0.25) \times 10^{-4}$ gram moles.

Using published data for the mass spectral pattern of CH_3D, where $17^+ = 100$, $16^+ = 77$, and the data already quoted for CH_4, we can write for a mixture of CH_4 and CH_3D that:-

Voltage of a peak at 16^+ = $x + 0.77\ y$, and

Voltage of a peak at 17^+ = $y + 0.011\ x$

where x = volts contributed at 16 mass units by CH_4, and

y = volts contributed at 17 mass units by CH_3D.

In the case of the experiment at 1120°K. this gave $(y/x + y)100$ equal to the percentage of CH_3D as 59%. By a direct calibration for CH_4 which it is reasonable to assume for this mixture, 0.238×10^{-4} gram moles of CH_4 and 0.346×10^{-4} gram moles of CH_3D were made. From experiments in nitrogen only 0.15×10^{-4} gram moles of methane would have been expected, so that the methane production when using

deuterium as carrier gas shows an excess over the expected value of 290%. If the CH_3D arises by the attack of a methyl radical on D_2, then there is no question of considering that 0.346×10^{-4} gram atoms of hydrogen were ejected from methane by an exchange reaction.

The evaluation of the analysis of the C_2 hydrocarbons used the relative intensity data for ethane and ethylene given in Appendix II, and the following observed voltages:-

Peak	31^+	30^+	29^+	28^+	27^+	26^+
Voltage	0.175	0.0483	0.087	0.532	0.1265	0.0935

If we assume that :-

(1) The contribution to the 30^+ voltage by C_2H_6 = x

(2) The contribution to the 31^+ voltage by C_2H_5D = y

(3) The contribution to the 28^+ voltage by C_2H_4 = p

(4) The contribution to the 29^+ voltage by C_2H_3D = q

the following equations can be constructed:-

(a) $0.0175 = y + 0.023\ x$

(b) $0.0483 = x + 0.788\ y + 0.022\ q$

(c) $0.087 = 0.788\ x + 3.31\ y + 0.022\ p + q$

(d) $0.532 = 3.31\ x + 0.967\ y + 0.648\ q + p$

(e) $0.1265 = 0.967\ x + 0.606\ y + 0.623\ q + 0.648\ p$

(f) $0.0935 = 0.606\ x + 0.0056\ y + 0.117\ q + 0.623\ p$

With only four variables this gives more than the necessary

TABLE XI

	Amounts made in moles x 10^4.		Percentage of Total Gas.	
	Expt.(1)	Expt.(2)	Expt.(1)	Expt.(2)
H_2	2.435	2.354	77.7	77.9
CH_4	0.238	0.210	7.6	6.9
CH_3D	0.346	0.336	11.1	11.1
C_2H_6	0.037	0.034	1.2	1.1
C_2H_5D	0.018	0.018	0.6	0.6
C_2H_4	0.054	0.058	1.7	1.9
C_2H_3D	0.008	0.012	0.3	0.4

	Percentage Deuterated.	
	Expt.(1)	Expt.(2)
Methane	59	62
Ethane	33	35
Ethylene	13	17

number of equations to provide solutions. It was decided not to use equation (d) since the 28^+ voltage has always a considerable correction applied to it for the background spectrum of the instrument. Using equations (a), (b), (e) and (f), we find that on solution:-

$q = 0.0149$, $p = 0.1133$, $x = 0.0348$, $y = 0.0167$.

Using mass spectral sensitivity data for ethylene and ethane, this gave the following data:-

Substance	C_2H_6	C_2H_5D	C_2H_4	C_2H_3D
gm.moles x 10^6	3.65	1.75	5.42	0.80

A second experiment under very similar conditions gave on analysis:-

Substance	C_2H_6	C_2H_5D	C_2H_4	C_2H_3D
gm.moles x 10^6	3.37	1.83	5.82	1.16

The total production of C_2 hydrocarbons was 11.7×10^{-6} gram moles and 12.2×10^{-6} gram moles respectively, of which 22% and 25% respectively were deuterated. Table XI summarises the findings for the gaseous products from the experiments with deuterium.

The evidence for extensive exchange of hydrogen and deuterium atoms, in the system where toluene decomposes in a deuterium carrier gas, was against the original project to use fluorene plus toluene mixtures as part of the kinetic investigation. However, it was considered worth while to

carry out one experiment with fluorene and deuterium to see whether the observed exchange reaction was also rapid for this compound.

A pyrolysis of 0.06 mm. fluorene in 6.00 mm. deuterium at 796°C. with contact time 0.601 seconds was carried out. As can be seen from the following data on the mass spectra of products and starting materials, there was considerable exchange:-

Peak at m/e =	165^+	166^+	167^+	168^+	169^+
Products relative intensities	79	100	33	63	25
Initial fluorene relative intensities	85	100	14.5	0.0	0.0

Since the mass spectra of deuterated fluorenes are not available, a full analysis of such figures cannot be made, but some valuable points can be gleaned. The ratio of relative intensities $169^+ / 168^+$ is too high to be explained by the usual C^{13} isotope peak and suggests at least some tri-deuterated fluorene (fluorene - d_3), accompanied by a substantial formation of fluorene - d_2. In the absence of cracking pattern data, it would be largely conjecture to go beyond this. If it was thought that the exchange occurred preferentially in the CH_2 group of the five ring, and if the mass spectrum of normal fluorene gave peaks at m/e = 165^+ and 164^+ for the reason that these are the most readily lost hydrogen atoms,

then one would predict that fluorene -d_2 would have a mass spectrum containing 168^+, 166^+ and 164^+ as major peaks. This behaviour could account for a lower peak height at m/e = 167^+ than at m/e = 168^+.

The hydrogen present as H_2 or HD amounted to 1.1×10^{-4} gram moles of which only 0.1×10^{-4} gram moles was expected from data with nitrogen as carrier gas. From the relative intensities in the solids spectrum, together with the total amount of fluorene used, it would be a legitimate rough estimate that 10^{-4} gram moles of hydrogen had been displaced by exchange processes.

THE LIQUID PRODUCTS.

The quantitative analysis for benzene, the only liquid product for which mass spectroscopic evidence was found, was complicated by its low proportion (about 1%) in the toluene, and the interference of the latter through its contribution to the mass spectrum at the peaks m/e = 77^+ and 78^+. The 78^+ ion gives rise to the largest peak in the benzene mass spectrum, and its relative intensity in the toluene mass spectrum is only 0.75% of that for the peak m/e = 91^+, yet the molar proportions in the pyrolysis product result in toluene and benzene making contributions of the same order to the product mass spectrum.

Two methods of analysis have been adopted. The first is the conventional use of the separate cracking patterns of toluene and benzene at the peaks m/e = 77^+ and 78^+ (see Appendix II) to set up simultaneous equations with the observed voltages for a sample. The other method was to establish an empirical graph relating the peak height ratio $78^+/91^+$ to the composition for a series of solutions of benzene in toluene, and to use these data for analysis. The methods are illustrated below for a

sample from a run at 847°C. on 24/9/56:-

Method I.

Observed peak voltages - 77^+, 0.0936; 78^+, 0.0685. Using the cracking pattern data for the actual toluene used as reactant (Appendix II) this gives equations:-

$$0.0936 = x + 0.143\,y$$

$$0.0685 = 0.51x + y$$

where x is the contribution from toluene to the peak m/e = 77^+, and y is the contribution from benzene to the peak m/e = 78^+. Solution of the equations shows that benzene contributed 0.0223 to the total voltage of 0.0685 for the 78^+ ion peak. By the use of sensitivity data, this was equivalent to 1.71×10^{-5} moles benzene produced during a run in which 4.713×10^{-3} moles of toluene were injected.

Method II.

The graph of the $78^+/91^+$ peak ratio for synthetic mixtures of benzene and toluene against weight per cent of benzene, gave a relationship (0.75 + 1.7(weight per cent benzene)) for this ratio. Using the observed value of 1.283 we obtain a weight per cent benzene in the product of 0.313 which is equivalent to 0.369 mole per cent or 1.74×10^{-5} moles in the 4.713×10^{-3} moles of toluene.

Using these methods, the following data were obtained:-

Run Date and No.	17/9/56. (1)	(2)	(3)	24/9/56	15/9/56
Moles Benzene x 10^5					
Method I	6.56	5.06	2.39	1.71	1.26
Method II	5.5	4.77	2.43	1.74	1.52

The agreement of methods I and II is satisfying in view of the intrinsic difficulty of the methods. Since method I uses the data on ions of mass number 77 and 78 plus the amount of toluene collected, while method II uses the data on the 78^+ and 91^+ ion peaks, the amount of collected toluene and an empirical calibration graph, there appears to be sufficient differentiation in procedure to justify a belief in the order of the results.

From the point of view of overall stoichiometry, the products containing the phenyl radicals (see page135) should be related to those containing the methyl radicals. In the case of the two runs, (2) and (3) on 17/9/56, the complete gas analyses are available for comparison with the benzene production. The details are given below:-

	Run (2) (Moles x 10^5)	Run (3) (Moles x 10^5)
Benzene (average)	4.91	2.41
Methane	3.67	3.11
2 x Ethane	0.39	0.33
2 x Ethylene	8.22	3.49
Ratio (Benzene/ Total "methyl")	0.39	0.35

The data shows a marked deficiency of benzene, and this seems to be due, in the main, to the quantity of ethylene detected. Due to the presence of nitrogen, the mass spectral analysis for ethylene was more difficult than for ethane, but its presence was quite evident, including the deuterated compound in experiments with deuterium as carrier gas. It is necessary, therefore, to consider the possible fates of phenyl radicals or other explanations.

One possibility is that the phenyl radicals added on to benzyl radicals or substituted into the nucleus of toluene in order to give the observed solid products of mass number 168 (see page 140). Another is that some of these radicals decomposed on the wall. In view of the low proportion of hydrogen in the phenyl radical, the low molecular weight hydrocarbons could only be obtained from such a decomposition

if a carbon deposit was formed. The kinetic data certainly indicate that a pre-coating of the reaction vessel walls was occurring. Allowing 2.5×10^{-16} sq.cm. per carbon atom, it would take 6.6×10^{-6} gram atoms of carbon to give only a monatomic layer on the hot wall of the reaction vessel. However, the deficiency in phenyl radicals is of the order of 10^{-4} gram moles if the ethylene is counted in and considered to come from ethane via methyl radicals. Quantities of carbon sufficient to account for this discrepancy were not observed experimentally. At the present stage, it does not seem profitable to pursue this aspect, as much further data would be required. The major inference is that the sample ratio (methane/benzene) = 1 is not obeyed as required by Szwarc.

Liquid Products from Runs in Deuterium Carrier Gas.

The analytical problems here were slightly different. Whereas in the previously described experiments, the liquid product showed only the usual relative intensity in the mass spectrum of 0.14 for m/e = 79^+ , the runs with deuterium as carrier gas gave a liquid product where the relative intensities, (on a scale 91^+ = 100) were:-

Runs on 18/9/56 at 847°C.	79^+	78^+	77^+
(1)	1.02	3.68	2.23
(2)	1.31	5.9	3.37

An extension of method II (page 127) was applied to the analysis and, in the absence of cracking pattern data for monodeuterobenzene in the mass spectrometer, this gives a first approximation to the problem.

From the data of the American Petroleum Institute and Rylander et al.[33] the contribution from a monodeuterated toluene to the 79^+ ions gives a relative intensity of less than one per cent. Since the concentration of C_7H_7D in the products was necessarily low, we ignore its contribution, and allow for the 0.14 relative intensity due to C_7H_8 when equating the observed intensity for 79^+ = (0.14 + 1.7 (weight per cent of C_6H_5D)).

The relative intensity at m/e = 78^+ has contributions from C_6H_5D, C_7H_8 and C_6H_6. By analogy with the calibration for benzene, the first of these will contribute to (parent ion - 1)$^+$, that is 78^+, 14.3% of the parent ion intensity, while the second will add 0.75. Thus we have to deduct in run (1), (0.75 + 0.143 (1.02 - 0.14)) = 0.87 from 3.68 to get the 2.81 relative intensity due to C_6H_6. Using the calibration data as before, 2.81/1.7 = 1.65 weight % or 1.93 mole % benzene. By use of the known

moles of toluene passed, we obtain:-

	Run (1)	Run (2)
C_6H_5D (Moles X 10^4)	0.304	0.41
C_6H_6 (Moles X 10^4)	0.96	1.73
Total (Moles X 10^4)	1.26	2.14
Moles "methyl" X 10^4 in $CH_4 + CH_3D$; $2(C_2H_6 + C_2H_5D)$; $2(C_2H_4 + C_2H_3D)$	0.82	0.79
Ratio (benzene/ Total "methyl")	0.65	0.38

These results are in accord with the previous data in showing that the phenyl radicals do not all yield benzene in this pyrolysis.

THE SOLID PRODUCTS.

After completion of the solid products handling system with associated circulating pump and heated inlet lines, as previously described (pages 91 to 96), scans of possible standard substances, and of the more involatile products of the toluene pyrolysis were obtained.

It was found from all the solid products examined that there was a small amount (up to 10% of the total) which proved too involatile to vapourise into the mass spectrometer at 100°C. Since this suggested a high molecular weight substance, the handling system temperatures were raised to 200°C. and the sample vessel torched. This produced no detectable change in the mass spectrum, or the production of ions of higher mass. The material itself eventually charred. An infra red spectrum of the material gave peaks at 1450 $cm.^{-1}$, 1259 $cm.^{-1}$, and rather broad absorptions at about 1099 $cm.^{-1}$ and 1019 $cm.^{-1}$. The first two possibly refer to C - H deformation frequencies, but the spectrum as a whole was uninformative. This may have been due to the low solubility of the substance in carbon tetrachloride and carbon disulphide. This latter fact, taken in

TABLE XIa.

Mass Spectral Pattern of Diphenylmethane.

Mass No.	Observed Voltages.	Relative Intensities.	A.P.I. Relative Intensities.
169	0.125	12.6	13.2
168	0.995	100.0	100.0
167	0.883	85.7	83.1
166	0.1375	13.8	12.4
165	0.2925	29.4	28.8
164	0.035	3.52	4.03
163	0.025	2.52	2.2
154	0.0435	4.37	1.71
153	0.1478	16.67	13.7
152	0.1828	14.85	16.3
151	0.0261	2.62	1.74

conjunction with its great involatility, suggests a polymerised substance of high molecular weight.

It is customary in the presentation of the mass spectral cracking patterns of the hydrocarbons, to express the results in the form of relative intensities of the peak heights at the various values of m/e, the value assigned to the most prominent peak being 100. The American Petroleum Institute, Project No.44, provides data of this type in tabular form for several hydrocarbons which are relevant for this work, although not for all those which are of interest. Since the cracking pattern does show minor variations which depend on the instrument used, the American Petroleum Institute data have been applied mainly for comparisons, and standard spectra determined on the St.Andrews instrument. As an illustration, voltages for various masses in the diphenylmethane spectrum were obtained and the relative intensities were calculated and compared with the American Petroleum Institute data as shown in Table XIa.

The table shows the measure of agreement usual for such comparisons of different instruments.

The broad qualitative features of the mass spectral patterns of the solid products are best shown diagrammatically as in Fig.(28), which also includes data for some pure materials which were considered to be possible constituents.

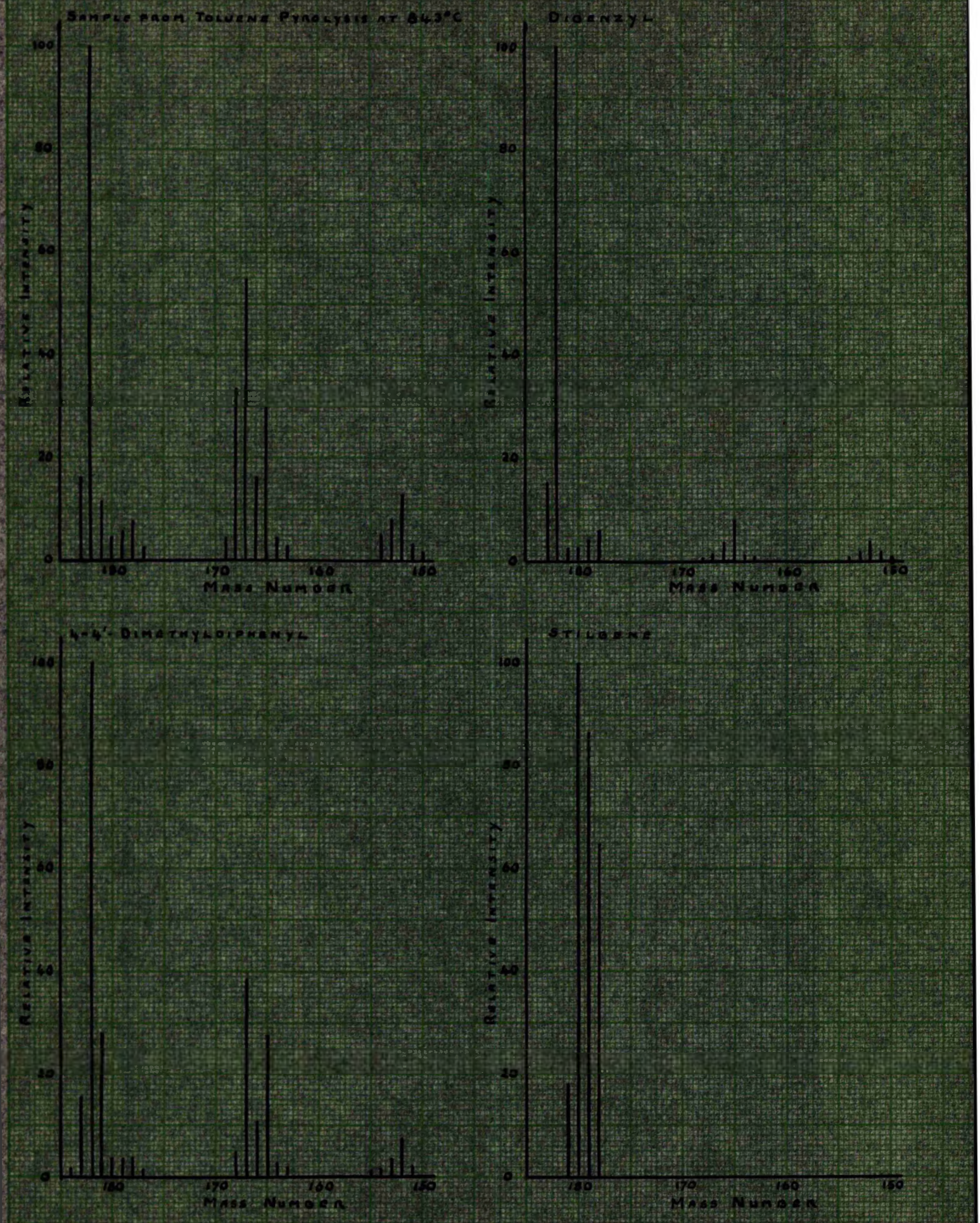

Sample from Toluene Pyrolysis at 843°C
Dibenzyl
4-4'- Dimethyldiphenyl
Stilbene
Relative Intensity
Mass Number
100
80
60
40
20
0
180
170
160
150

FIGURE (28).

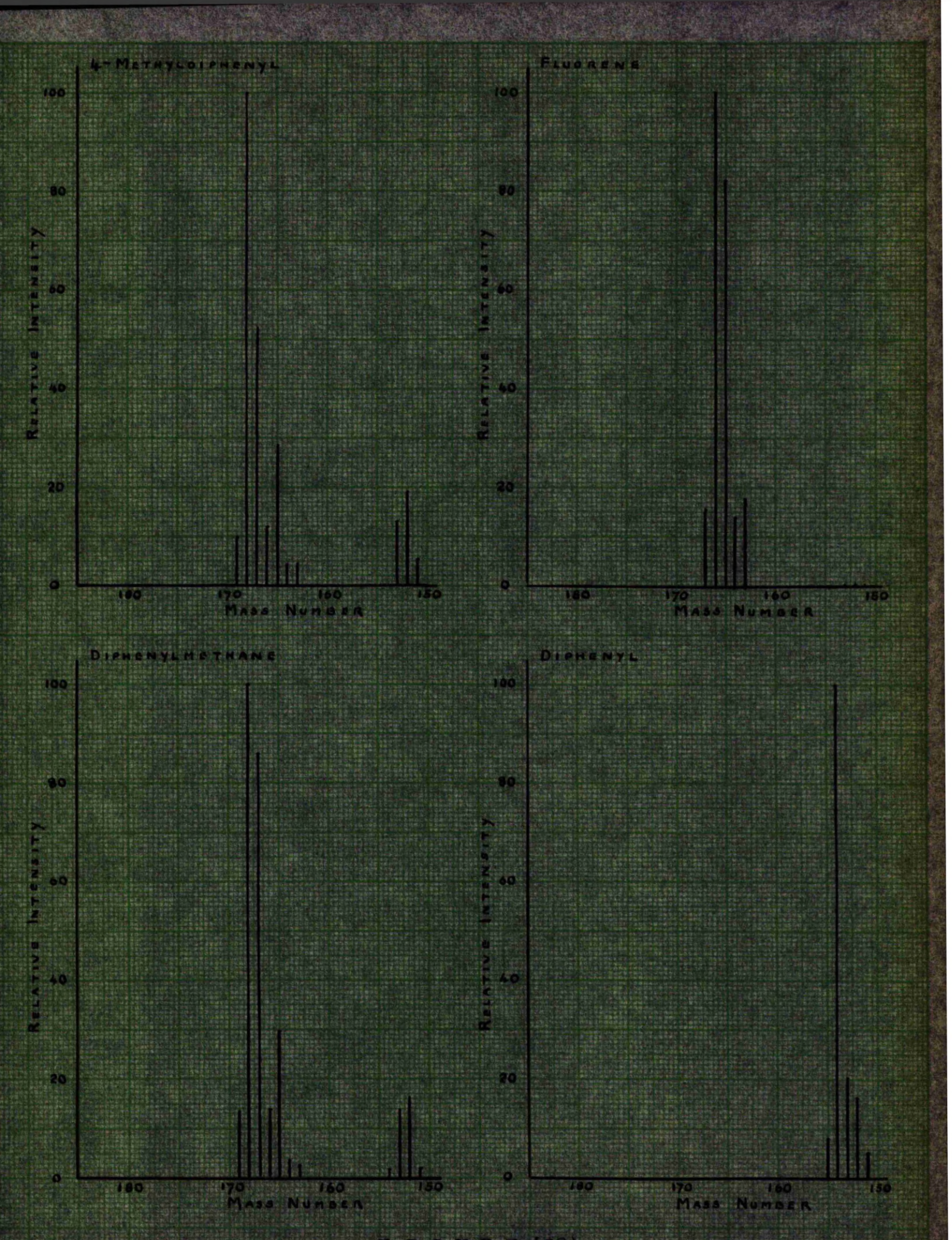

4-Methylbiphenyl
Fluorene
Diphenylmethane
Diphenyl
Relative Intensity
Mass Number
100
80
60
40
20
0
180
170
160
150

FIGURE (28).

The pattern shown was that for the solids derived from the pyrolysis of toluene at 843°C. at a pressure of 1.5 mm. toluene and contact time of 0.69 seconds.

The first feature which is strikingly evident is the presence of substantial peaks corresponding to masses in the 168 and 153 mass number regions. These peaks are not evident at all in the mass spectrum of dibenzyl, which was claimed by Szwarc to be the only solid product. As can be seen from the diagrams, peaks in these regions can be derived from dimethyldiphenyls, monomethyldiphenyls, diphenylmethane, fluorene and diphenyl. In attempting to establish more definitely the origins of the product peaks, some of the finer differences of the patterns from these compounds have to be noted.

Under electron impact, dimethyldiphenyls, (which have molecular weight 182), can lose one or two methyl groups and give masses 167 and 152 in reasonable amounts. They actually produce a small collection of peaks in these regions with those named as the most prominent.

The monomethyldiphenyls (molecular weight 168), give the highest intensity for the parent molecular ion, and can also yield ions in the 152 mass number region.

The salient distinction between these two classes of compound in the 168 region, is that the monomethyl compounds

have a high intensity at m/e = 168^+, while the dimethyldiphenyls have as their highest peak in this region m/e = 167^+. It is obvious, therefore, that in dealing with the mass spectral patterns of the products the methods of assigning the mass numbers have to be checked carefully for accuracy.

Methods for Mass Number Assignments.

The most convenient method for our purposes was to add to a sample under investigation some conveniently handled compound, the mass spectrum of which was known. This would then produce an augmentation of the heights of known peaks, or would produce a peak of mass number M_1 focussed with a particular magnet current and an accelerating voltage E_1. If the magnet field strength was not altered the mass number M_2 of any other peak would be expected to occur at an accelerating voltage E_2, such that $M_1 / M_2 = M_2 / E_1$.

The first attempt to use this technique employed methyl iodide, which has a major peak in its spectrum at m/e = 142^+. As a preliminary test, methyl iodide and diphenylmethane were examined together. The 168 mass number peak of diphenylmethane was focussed at 1600 volts accelerating potential, and electrostatic scanning found the main peak of the methyl iodide at 1865 volts. Now 1600/1865 = 144/168, instead of the required 142/168. Indeed, the voltage which should have been observed

TABLE XII.

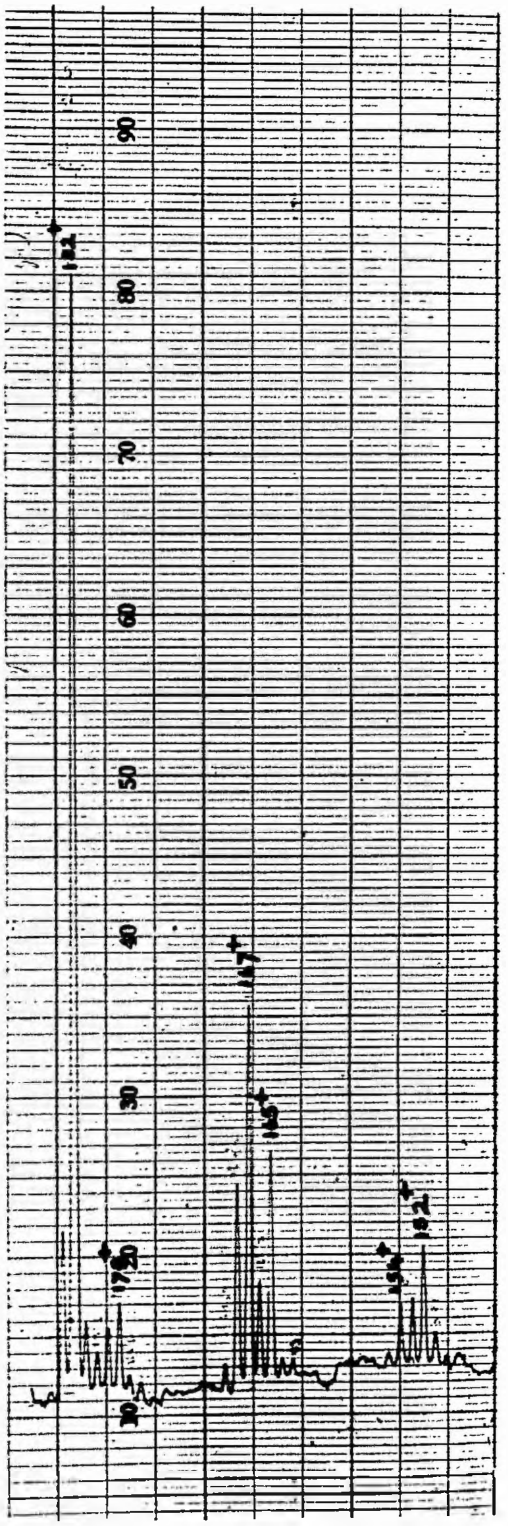
Suggested Mass No.	Peak height of mixture minus Peak height of sample.	Relative Intensity (168^+ = 100)
169	0.0325	14.6
168	0.223	100.0
167	0.19	85.3
166	0.0415	18.6
165	0.0742	33.3

for the methyl iodide parent peak was 1893 volts.

The discrepancy of 28 volts was much greater than the reading error on the voltmeter (about $\pm$ 2 volts) and the instrument itself did not have such an error. On repeating the experiment, the discrepancy became 7 volts, and it was found that during the interval of time required to scan from the diphenylmethane to the methyl iodide peak the magnet current had changed slightly. It was considered that this hazard was sufficient to rule out methyl iodide as a mass marker, and that a compound giving peaks identical with, or very close to the unknown ones was required. As a second choice diphenylmethane was used, which gives four major peaks in the region 165^+ - 168^+, and which were superimposed on the peaks from the samples in that region. While permitting an undoubted mass number assignment for peaks in this region, the use of this compound did involve the performing of two separate scans, one before and one after its addition, and in order to be certain of the numbering, an evaluation of the data on the lines given in Table XII.

It can be seen that the last column is in excellent agreement with the standard data for diphenylmethane given in Table XIa.

It was decided later to use p-bromotoluene as the



F I G U R E (29).

additive since it gives peaks at m/e = 170^+ and 172^+, due to the isotopes of bromine, and from these it was easy to count back down the mass number scale to the 167 region.

For the 152 mass region, diphenyl was used as a marker.

RESULTS.

Qualitative Treatment of the Data.

The mass spectral data on the solid products are given in Appendix II in terms of the relative intensities of the peaks of interest on a scale where the voltage at 182 mass units has been taken as 100. For convenience in description and deduction the groups of peaks in the 182, 168 and 152 regions will be treated separately. A typical mass spectrum of the solid products is shown in Fig.(29).

The mass peak corresponding to 183^+ was the highest observed and is most probably the carbon isotope peak for hydrocarbons of molecular weight 182. The normal isotopic abundance of C^{13} is 1.1% and for a hydrocarbon with fourteen carbon atoms, this means that the isotope peak is about 15 - 16% of that for the parent molecule. For the samples observed the ratio of peak heights (183^+ / 182^+) was 11.5 to 17.5, and since the actual peak heights for 183^+ were

only about 20 millivolts, the errors due to shifts in amplifier zero would produce much of this variation.

The relative intensities of the 181^+ peak in the products from pyrolyses at the following temperatures were:-

864°C. 10,19; 831°C. 6.5, 8; 799°C.9.3, 11.5, 6.7.

The same comments on the errors due to the very small peak heights apply to this also. If an average value of (100/10.3) is taken for ($182^+/181^+$), this can be compared with (1002) for pure dibenzyl and (100/27.7) for 4-4'-dimethyldiphenyl. This would suggest that a mixture of the two compounds could produce the observations.

If we continue down the mass unit scale, the possibility of stilbene being a significant contributor can be ruled out. Taking the relative intensities of the various ionic masses for the solid products of a pyrolysis experiment at 843°C. they can be compared as follows with standard mass spectra:-

Peak at m/e =	183^+	182^+	181^+	180^+	179^+	178^+
Solid Product	16	100	11.2	4.17	5.13	7.05
Dibenzyl	16	100	1.99	3.67	5.73	1.59
4-4'-Dimethyldiphenyl	15.6	100	27.7	3.17	3.05	3.53
Stilbene	-	-	15	100	86.6	64.7

TABLE XIII.

4-MDP	=	4-Methyldiphenyl
3-MDP	=	3-Methyldiphenyl
2-MDP	=	2-Methyldiphenyl
4-4'-DMDP	=	4-4'-Dimethyldiphenyl
DPM	=	Diphenylmethane
DB	=	Dibenzyl

Mass Number	169	168	167	166	165	164	163
4-MDP	14.9	100	52.2	11.8	28.7	4.26	4.26
3-MDP	14.4	100	42.9	7.9	18.8	1.9	1.73
2-MDP	14.1	100	72.3	12.8	30.4	3.31	3.01
DPM	12.6	100	85.7	13.8	29.4	3.52	2.52
4-4'-DMDP		100	781.0	222.0	565.0	55.0	35.0
(above on 182^+ = 100)	(0.7)	(4.88)	(38.15)	(10.85)	(27.55)	(2.68)	(1.71)
DB (182^+ = 100)		(0.4)	(1.1)	(3.45)	(7.83)	(0.85)	(0.65)
(168^+ = 100)		100	275.0	862.0	1960.0	212.0	162
Product ex.expt. at 843°C. (168^+ = 100)	11.9	100	163.0	48.5	87.5	12.9	8.58
(above on 182^+ = 100)	(4.0)	(33.6)	(54.8)	(16.3)	(29.5)	(4.33)	(2.88)

If stilbene was a prominent contributor to the figure for 181^+, then the 180^+ peak could hardly fall in the way observed, and the figures for 179^+ and 178^+ would be expected to be higher also. This view that stilbene need not be considered was reinforced by consideration of the ultra violet absorption spectrum of the solid products. Both stilbene and the dimethyldiphenyls have absorptions giving extinction coefficients of over 10,000, but the curve for the former gives a flat maximum at about 2950 A, while the latter has a similar rounded maximum at 2550 A. Dibenzyl, of course, is a weak absorber in the ultra violet. The absorption curve for the solid products had a maximum near 2600 A, and by 3000 A the absorption had become very low. There seems to be no reason, therefore, to consider stilbene to be a significant constituent of the solid products.

The next region of the mass spectrum of interest lies from mass units 163 to 169, and it is convenient to consider the relative intensities on a scale with the value for 168^+ taken as 100. In this part of the spectrum, the contribution of dibenzyl does not rise above 8% of its value at 182^+. The most probable contributing substances appear to be dimethyldiphenyls, monomethyldiphenyls and diphenylmethane. The relative intensities at various mass numbers are shown in Table XIII.

TABLE XIV.

Mass Number	154	153	152	151
Dibenzyl	100	290	740	330
4-4'-Dimethyldiphenyl	100	264	570	136.5
4-Methyldiphenyl	100	492	736	193
3-Methyldiphenyl	100	815	1253	218
2-Methyldiphenyl	100	746	638	105
Diphenylmethane	100	802	953	102
Diphenyl	100	20.3	16.6	5.06
Product ex. expt. at 843°C.	100	165	256	64.5

As with the previous region, the highest mass (169) appears to be a C^{13} isotope peak, with the parent molecules of the first four entries providing the molecular ions 168^+. In the entry for 4-4'-dimethyldiphenyl it has to be noted that the parent fragment is probably of mass 167, and the ($168^+/167^+$) ratio corresponds to a 13% isotopic peak.

By comparison of the solid pyrolysis product spectrum with the other data, it can be seen that the intensities of all peaks from 163^+ to 167^+ are higher relative to 168^+ than the same quantities for any monomethyldiphenyl or diphenylmethane. Therefore, these compounds would need to be present in admixture with dimethyldiphenyl which has a high $167^+/168^+$ ratio, in order to obtain figures of the type of the product sample.

Continuing down the scale of mass numbers, the next group of peaks for m/e = 150^+ to 155^+ ions are smaller in size than those already treated. Contributions to them can arise from the compounds already discussed, and diphenyl could be an additional contributor. The data can be summarised as before, but it is now convenient to take the 154^+ ion intensity as 100 as in Table XIV.

It can be seen by inspection of this Table that the rise in relative intensities in the sequence 154^+, 153^+, 152^+

TABLE XV.

	Relative Intensities of 91^+ ions.
Dibenzyl (182^+ = 100	360 - 440
4-4'-Dimethyldiphenyl (182^+ = 100)	9.26
4-Methyldiphenyl (168^+ = 100)	14.9
3-Methyldiphenyl (168^+ = 100)	5.77
2-Methyldiphenyl (168^+ = 100)	5.52
Diphenylmethane (168^+ = 100)	51.4
Diphenyl (154^+ = 100)	-
Product ex.expt. at 843°C. (182^+ = 100)	238

is much greater for the mono and dimethyldiphenyls and for dibenzyl than it is for a typical product sample. Since the behaviour of intensities in the diphenyl spectrum follows a reverse trend, it is an obvious possibility that a mixture which includes a suitable proportion of diphenyl might reproduce this behaviour. The proportion need not be large since only diphenyl is a major contributor in this region.

The final part of the spectrum to be considered is the 91^+ region where the peak m/e = 91^+ is more than twelve times the height of its neighbours. The most significant feature here is the relative intensity of this peak with respect to the parent molecule ion as shown in Table XV.

The contributions of all compounds save dibenzyl and diphenylmethane are negligible, and that of the former predominates. As a rough assessment, we note that the proportion $91^+/182^+$ in the pyrolysis product is about half of that in dibenzyl, which suggests that the product may contain about this proportion of that substance. Furthermore, in experiments where the $91^+/182^+$ ratio is above average, the intensity of peaks in the 168 region is below average. This suggests that a course of reaction which leads to dibenzyl occurs at the expense of one leading to methyldiphenyls.

Quantitative Treatment of Data.

In order to make more precise deductions, we have to consider the relative sensitivities of the compounds to disintegration under electron impact. This is often quoted by giving the ion current for the most prominent peak in the mass spectrum of a compound when compared with, say, the 43^+ ion peak in n-butane, each being at the same reservoir pressure. This is the form of treatment given in the compilation of mass spectra by the American Petroleum Institute, and merely serves as a method of comparison, since sensitivities change with the instrument and with the condition of any one instrument. The most direct form of quantitative mass spectroscopy uses calibrations done at the same time or immediately after the analysis of the sample. With substances that are gaseous at ordinary temperatures, the measurement of the necessarily minute quantities of calibrating materials can be done accurately, and an injection performed into the sample under examination before the latter is withdrawn. With solid substances the difficulties of such a procedure are much greater, and considerable work on calibration would have been needed with all the possible substances if precise analyses were to be achieved.

A recent suggestion to assist in overcoming such troubles

is to make use of the fact that the sum of the ion intensities of the peaks in a mass spectrum is approximately proportional to the sum of the valence electrons in a compound. The basis of this seems to lie in the ideas put forward by Eyring[46] that the disintegration fragments are formed from a parent molecular ion resulting from an electron impact. The chance of forming such an ion is proportional to the sum of the atomic ionisation cross sections for a molecule. In an analysis of these ideas in terms of experimental data, Hood[47] has noted the differences produced by aromatic and saturated ring systems of increasing complexity, and of paraffinic chain length. From the point of view of this work, the significance is that the total ion intensity will be very similar for such compounds as dibenzyl and dimethyldiphenyls, which have two aromatic rings and total composition $C_{14}H_{14}$. In addition, the ratio of the total ion intensities for such compounds and those of formula $C_{13}H_{12}$ can be calculated using the empirical expression of Otvos and Stevenson[48], that the total ion intensities are proportional to (number of hydrogen atoms + 4.16 x number of carbon atoms). This gives a ratio of 72/66 for this case.

The above section only discusses the total ion intensity produced from substances. In actual analyses the intensities

of particular mass peaks are required, and can be obtained by use of the cracking pattern expressed in terms of relative intensities. When considering mass spectra in the 163 - 169 mass units region, it is convenient as stated earlier, to work out the data using mass number 168 as the base peak, that is, assigning it a relative intensity of 100. The relative sensitivity of dibenzyl to a dimethyldiphenyl at mass number 168 can be defined as being equal to :-

$$\frac{\text{Ion current at } 168^{+} \text{ due to dibenzyl}}{\text{Ion current at } 168^{+} \text{ due to dimethyldiphenyl}}$$

In the spectrum of dibenzyl, the relative intensity of 168^{+}, (182^{+} = 100) is 0.4, while for 4-4'-dimethyldiphenyl it is 4.88. The sum of the relative intensities of all the ions from dibenzyl is 806, while for 4-4'-dimethyldiphenyl it is 463. Thus the proportion of the total fragment ions of dibenzyl which is of 168 mass units is (0.4/806), while for 4-4'-dimethyldiphenyl it is (4.88/463). If, by the previous argument, the total ion intensity was the same for these $C_{14}H_{14}$ compounds, then the relative sensitivity at 168 mass units for dibenzyl to 4-4'-dimethyldiphenyl is (0.4 x 463/4.88 x 806) = 0.0472. In the case of dibenzyl and monomethyldiphenyl, the total ion intensity of the former

was taken to be (72/66) times that of the latter, and the relative sensitivity was deduced to be (0.4 X 450 x 72/ 100 x 806 x 66) = 0.00244. From this data we see that if, under standard conditions, a certain concentration of dibenzyl gave an ion current I for m/e = 168^+, then the currents from the same pressure of di- and monomethyldiphenyl would be (I/0.0472) and (I/0.00244). For a mixture of dibenzyl, dimethyldiphenyl and monomethyldiphenyl of mole fractions a, b and c the total ion production at 168^+ would be I(a + b/0.0472 + c/0.00244).

At any other mass number we have to consider the cracking pattern of the substance on a scale with the 168^+ ion intensity for each compound taken as 100. Let x, y and z be the relative intensities at m/e = M^+, then the total ion production at that mass number for the above mixture will be:-

I(a.x + b.y/0.0472 + c.z/0.00244).

This permits the deduction for the mixture of the relative intensity (P) for m/e = M^+ relative to 168^+ taken as 100:-

$$P = \frac{(a.x + b.y/0.0472 + c.z/0.00244)}{(a + b/0.0472 + c/0.00244)}$$

In this formula x, y and z are known but a, b and c have to be found or estimated.

There are two ways of using this formula. Experimental

values of P, x, y and z for one mass number can be inserted, and an equation in a, b and c as unknowns produced. By using the data appropriate to two other mass numbers one can obtain two further equations. If only three constituents are considered this is quite sufficient to permit a solution for the unknown molar fractions. The further relationship $a + b + c = 1$ is also available. The method requires accurate cracking pattern data for specific compounds, and since the number of $C_{14}H_{14}$ and $C_{13}H_{12}$ compounds which can be considered is large, the equations could contain many unknowns and be intractable for solution.

It was felt to be more in keeping with the requirements and the complexity of the problem if some of the molar proportions were estimated, and the chosen values of a, b, c etc., applied to calculate the relative intensity P in complicated parts of the spectrum.

In order to obtain approximate values for the molar fractions, and to apply these to calculate trial values of P at several mass numbers, it was first assumed on the basis of the earlier qualitative reasoning that the pyrolysis product was formed mainly from dibenzyl (a), 4-4'-dimethyldiphenyl (b), and 4-methyldiphenyl (c). Taking a pyrolysis product at 811°C., where for m/e = 167^+, P = 204, x = 275, y = 781, and z = 52.2, and for m/e = 91^+, P = 1933, x = 110,000, y = 190

TABLE XVI.

DB = Dibenzyl
DMDP = 4-4'-Dimethyldiphenyl
MMDP = 4-Methyldiphenyl

Mole Fractions.			Relative Intensities				
DB	DMDP	MMDP	167	166	165	164	91
0.5	0.5	-	788	251	628	62.2	-
0.5	0.4	0.1	178	55.9	139	14.9	1144
0.4	0.45	0.15	151	44.7	111	12.2	653
0.6	0.32	0.08	140	35.3	148	15.6	1687
Product ex. expt. at 811°C.			206	57	114	-	1933
Product ex. expt. at 831°C.			183	51.5	103	-	1435

and z = 14.9, all being on the basis of m/e = 168^+ having intensity 100, we obtain by combination with a + b + c = 1, the solutions a = 0.624, b = 0.305, c = 0.071. This particular experiment had a higher $91^+/182^+$ ratio than some others which would be satisfied with a dibenzyl mole fraction of about 0.5.

These calculations suggest that the solid product is about half dibenzyl with the dimethyldiphenyl and monomethyldiphenyl in the ratio 4/1 approximately. In order to check the latter point more extensively, values of P have been calculated from the formula (page 146) for the peaks m/e = 167^+, 166^+, 165^+ and 164^+. The results are compared with some product data in Table XVI.

One of the points emerging very clearly is the need to include a small amount of monomethyldiphenyl (or something with a similar cracking pattern) in order to get synthesised figures approximating to the actual analyses. This can be seen by comparing the first two lines of the Table XVI. By comparing the second and fourth lines it can be seen that the main effect of a change of dibenzyl proportion is on the proportion of the peak m/e = 91^+, and not on the relative peak heights in the 164 - 167 mass region. The table shows that these are determined by the (dimethyldiphenyl/monomethyldiphenyl) ratio.

TABLE XVII.

DB = Dibenzyl
DMDP = 4-4'-Dimethyldiphenyl
MMDP = 4-Methyldiphenyl
DP = Diphenyl

Mole Fractions.				Relative Intensities			
DB	DMDP	MMDP	DP	154	153	152	151
0.5	0.4	0.1	-	100	329	642	181
0.5	0.4	0.09	0.01	100	137.5	256	72.7
0.5	0.39	0.09	0.02	100	92.3	163	46.8
Product ex expt. at 811°C.				100	150.5	276	75.3
Product ex expt. at 832°C.				100	107.5	187.5	50

When the 152 - 154 mass region was considered earlier, we noted that the product analyses suggested the presence of diphenyl. That the three component compositions considered above are inadequate for the description of the mass spectrum in this lower region can be seen by comparing the top and bottom lines of Table XVII. This gives the calculated cracking patterns for some mixtures derived by application of the formula (page 146) extended to cover four components. The relative sensitivity of dibenzyl to diphenyl, when taking the peak m/e = 154^+ as 100 was calculated by the method outlined previously, as being:-

$$\left(\frac{0.5}{806} \times \frac{72}{59.9} \times \frac{267}{100}\right) = 0.00199.$$

The proportion of diphenyl required to bring the synthesised cracking patterns within the range of the product compositions was very low as shown by the second and third lines of the table, where figures for one and two mole percent diphenyl are given. It is clear also from these results that the relative intensities are very sensitive to the amounts of diphenyl. In fact, when working out the formula, the term in the denominator referring to diphenyl determined the order of the result.

The conclusions from this analysis are as follows.

The solid products volatilised into the mass spectrometer appear to contain about 50 - 60 mole percent dibenzyl, 1 - 2 mole percent diphenyl and the remainder, dimethyldiphenyls and monomethyldiphenyls in the ratio of about 4/1. In the calculations given here, only data for 4-4'-dimethyldiphenyl and 4-methyldiphenyl have been used, but the cracking patterns for the other monomethyl isomers are similar to that of the one used, and it is probable that the same applies to the other dimethyldiphenyls. In these considerations, diphenylmethane has to be grouped with the monomethyldiphenyls, particularly in the 163 - 168 mass units region of its mass spectrum, and the presence of this compound would not greatly alter the general proportions of the solid products, since its mass spectrum is very similar to that of 4-methyldiphenyl, see Appendix II.

Apart from this analysis of the proportions of the different compounds formed, it was not possible in the time available, to study the quantitative yield of the solid products in an adequate fashion. The analysis given previously is a necessary preliminary to any more detailed treatment, and a brief attempt to extend the data was made in the following way.

The sum of the relative intensities of ions produced

is 806 for dibenzyl and 463 for 4-4'-dimethyldiphenyl. For each of these compounds the peak for m/e = 182^+ is taken to be 100, and so the sensitivity ratio at m/e = 182^+ is:-

$$\frac{\text{Dibenzyl}}{\text{4-4'-Dimethyldiphenyl}} = \frac{100}{806} \times \frac{463}{100} = 0.575$$

This value was confirmed by a direct measurement where, under comparable conditions, the sensitivity of dibenzyl = 0.0124 volts/mgm., while that of 4-4'-dimethyldiphenyl = 0.027 volts/mgm.

If we accept the fact that the molar proportions in the solid were 0.5 dibenzyl, 0.4 dimethyldiphenyl, and that the sum of all the ions made is the same for these two compounds, then the ratio of the voltage at m/e = 182^+ caused by dibenzyl to that caused by dimethyldiphenyl was

$$\left(0.5 \times \frac{100}{806} \Big/ 0.4 \times \frac{100}{463}\right) = 0.718.$$

Therefore the proportion of any voltage V at m/e = 182^+ due to dibenzyl was (0.718/1.718)V. The only other datum required for evaluation of the amount of dibenzyl was the mass spectral sensitivity to dibenzyl expressed as X volts/mgm. under the same electronic conditions as for the sample. If the number of moles of dibenzyl was Y, then the total solid was (Y x 1/0.5) moles, since it was present at 0.5 mole fraction.

Using this method on a few samples, the highest recovery of solid obtained was 63% of the amount of hydrogen produced. This figure was only of a preliminary character as time did not permit an extension of the experiments, but it is interesting to note that while Szwarc considered his "dibenzyl" was about equivalent in amount to the (hydrogen + methane), other investigators have not been so successful. Steacie et al.[6] quote a molar ratio (hydrogen + methane)/ non-volatile solids = 1.49/1.10, and Genco et al.[7] said the solids they weighed were always less than the combined hydrogen and methane expressed in moles.

Since this work has made it possible to obtain analyses for the solids, it would be valuable if further work could establish the stoichiometry of this aspect of the reaction more thoroughly. It is possible for example, that decomposition of phenyl radicals could supply some of the hydrogen. However, in view of the complexity of the solid products which we have shown to exist in the same temperature region as Szwarc's work, it is certainly doubtful whether it would be possible to establish a simple mechanism. As emphasised elsewhere (page 181), the gain in clarity of interpretation which occurs when a reaction mechanism leads to simple products is considerable. In the case of toluene, we judge that the considerable effort needed to establish a reasonable stoichio-

metry might not lead in the end to the identification without question of a rate determining step in the process. From the point of view of bond dissociation energy determinations this is a crucial requirement.

PYROLYSIS OF FLUORENE AND TOLUENE MIXTURES.

The experiments with deuterium as a carrier gas had removed the possibility of comparing the rate of any hydrogen atom reactions with that of:-

$$H + D_2 = HD + D$$

by a competitive process. There still remained, however, the question of testing the possibility of the reaction:-

$$C_6H_5CH_3 + H = C_6H_6 + CH_3$$

under the pyrolysis conditions; and for this purpose, the admixture of the more easily decomposed fluorene with the toluene was still of interest.

Before dealing with the mixture of substances, many separate pyrolyses of fluorene and toluene were carried out in the course of the development of techniques. Some of this work has already been described when dealing with the thermal conductivity gauge method of following the reaction. In the case of both substances, it was essential to season the reactor thoroughly before taking kinetic data, as described on page 103.

With emphasis on seasoning the reactor and not admitting oxygen when the reactor was hot, it was possible to obtain consistent behaviour.

TABLE XVIII.

Run.	Toluene. (Moles$_3$ x 10^3)	Fluorene. (Moles$_4$ x 10^4)	Hydrogen. (Moles$_5$ x 10^5)	Methane. (Moles$_5$ x 10^5)	Time of Run. (Mins.)	Time of Contact. (Secs.)
2	2.02	-	0.637	0.287	10	0.831
6	-	2.29	1.85	-	10	1.159
7	3.75	2.29	4.38	0.97	T.12 F.10	0.881
4	-	3.25	3.09	-	10	1.034
7	4.97	-	3.63	1.17	10	0.853
8	5.05	2.60	6.81	1.93	T.10 F.8	0.862
3	-	3.58	3.34	-	10	1.26
5	5.49	-	3.54	1.23	10	0.823
6	5.34	2.86	6.56	1.87	T.10 F.8	0.858
3	-	3.43	3.22	-	10	1.17
5	5.74	-	3.19	1.32	10	0.892
6	5.74	2.74	6.40	1.66	T.10 F.8	0.841

TABLE XVIII.

Furnace Temp. °C.	Expected H_2 (Moles x 10^5)	Expected CH_4 (Moles x 10^5)	(Increase in H_2/Expected H_2) x 100	(Increase in CH_4/Expected CH_4) x 100	Run.
796	2.66	0.57	64.7%	70.0%	2
796					6
796					7
800	5.82	1.22	17.0%	58.2%	4
800					7
800					8
800	5.41	1.25	21.3%	49.6%	3
800					5
800					6
801	4.85	1.25	31.1%	52.8%	3
801					5
801					6

The experiments with the two substances together were very troublesome and exacting technically. The scheme of experiment (see page 100), was to do a set of three runs, first a blank run with fluorene, then a blank run with toluene and, finally, a joint run with both substances. Apart from the usual experimental hazards, the task of controlling the temperature of two injection baths and the reactor, and manipulating a triplicate collection system was difficult for one person. The results of the runs are summarised in Table XVIII.

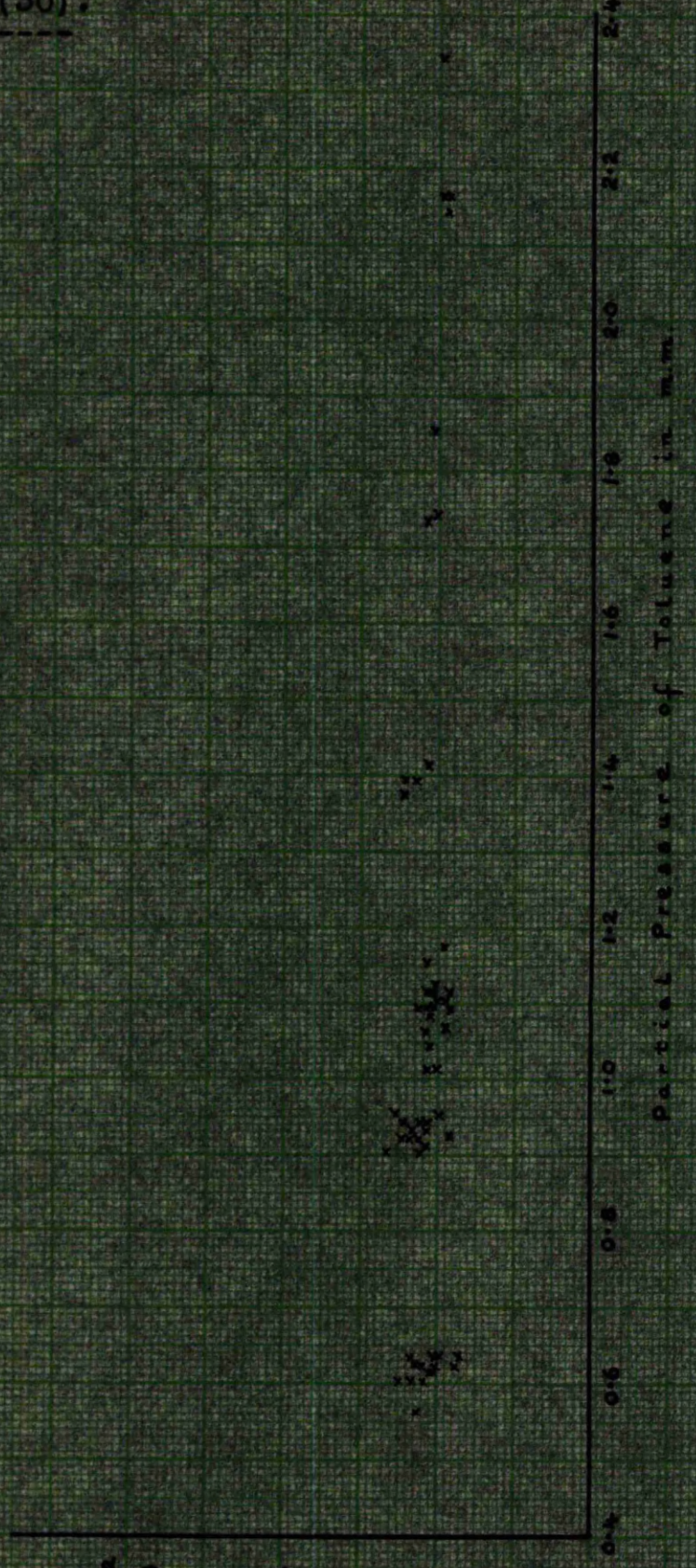
It can be seen from the data that significant rises in methane production were obtained. The fluorene was only present to about 6 - 10% of the toluene, but since it is more readily decomposed, it gave about the same amount of hydrogen in its blank pyrolysis. If the sequence of reactions in the mixture were uncomplicated, we might have anticipated some reduction of hydrogen production if the reaction:-

$$C_6H_5CH_3 + H\cdot = CH_4 + C_6H_5CH_2\cdot$$

removed hydrogen atoms. However, it is evident from the results that both hydrogen and methane were increased in amount, the latter to a greater extent. The increase in methane supports the existence of the above reaction. The increase in hydrogen suggests that the increase in

concentration of its atoms during the pyrolysis causes some sequence of reactions resulting in its further production. This throws some doubt on the use of (hydrogen + methane) production as a measure of primary processes in toluene pyrolysis. This point was not observed by Steacie et al. Perhaps it is of significance in this connection that when toluene has been used as a radical trap in pyrolyses, at temperatures where its decomposition on its own is negligible, the free radicals seem to induce some decomposition to methane and hydrogen. For example, in the case of benzil, which yields only phenyl and benzyl radicals, the toluene carrier gas shows some slight degree of sensitised decomposition.

FIGURE (30).


Partial Pressure of Toluene in mm
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
$\mu \times 10^4$ (sec^{-1})

EXPERIMENTS ON THE KINETICS OF THE REACTION.

The work of Steacie et al.[6] had shown that there was some doubt whether the decomposition of toluene followed a first order rate law, and in particular they had shown that there was a considerable variation of the first order velocity constant with change in the time of contact.

It was decided to repeat the investigation of the order of the reaction and, accordingly, two sets of experiments were performed, the first of which was a study of the variation of a first order rate constant with change in the partial pressure of toluene.

A change in the partial pressure of toluene was easily obtained by altering the temperature of the bath surrounding the toluene injection reservoir, and the time of contact was maintained reasonably constant by adjustment of the pressure of nitrogen in the system. The experiments were performed as described on page 97, and first order velocity constants

$$k_{(sec.^{-1})} = \frac{2.303}{\text{time of contact}} \log_{10} \frac{100}{100 - \% \text{ decomposition}}$$

calculated on the basis of the total (hydrogen + methane) produced. The results were expressed graphically, Fig.(30),


Rate of Flow of Toluene (Moles per second) x 10⁸
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
10
20
30
40
50
60
Bath Temperature °C.

FIGURE (31).

the two variables being the partial pressure of toluene and the velocity constant, and it can be seen that for a four-fold change in the partial pressure of toluene - from 0.56 to 2.34 mm. - the change in the velocity constant is small being from 0.00987 to 0.01136 second^{-1}. For twenty-six of these experiments the contact time was constant to within $\pm$0.1 second, and for another thirty experiments, the contact time was constant to within $\pm$ 0.2 second centred on 0.698 second. These experiments were performed over a considerably wider range of partial pressures than those used by Steacie, and show that for the time of contact used, the first order velocity constant is not dependent on the concentration of the toluene.

Secondly, experiments were performed to determine whether a first order velocity constant was dependent on the time of contact. In the type of flow system used, the time of contact could be altered by changing the pressure and, therefore, the rate of flow of the carrier gas. This, however, would produce an alteration in the partial pressure of the toluene, and since a constant toluene concentration was required, the temperature of the injection reservoir had also to be varied.

In order to eliminate the necessity for several preliminary experiments to determine the bath temperature

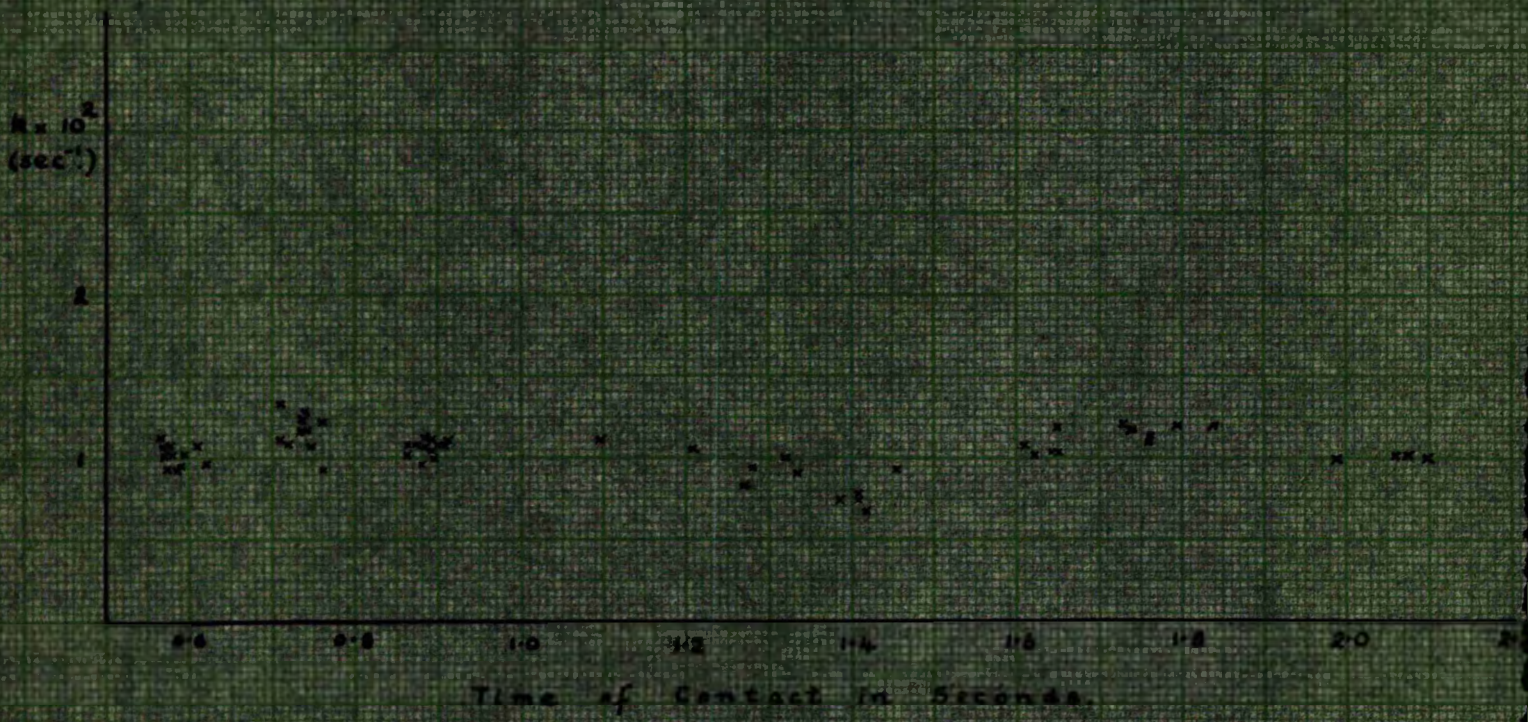


FIGURE (32).

required to produce a given partial pressure of toluene in a given pressure of carrier gas, toluene was injected into the flow system for a known time, collected and weighed, and the experiment repeated for several temperatures of the bath surrounding the reservoir. The rate of flow of the toluene in moles per second was calculated, and a graph plotted with this quantity and the bath temperature as variables, see Fig.(31). Then the required bath temperature to produce a set partial pressure of toluene for a given rate of flow of nitrogen and total pressure in the reactor could be obtained from this graph and the following relation:-

$$\frac{\text{Rate of flow of toluene}}{\text{Rate of flow of nitrogen + toluene}} = \frac{\text{Partial pressure of toluene}}{\text{Reactor pressure}}$$

The range of times of contact used was 0.565 to 2.076 second, and the partial pressure of toluene was constant within $\pm$0.21 mm. centred on 0.96 mm. It was unfortunately not possible in the apparatus used to reach lower contact times and keep the toluene concentration reasonably constant, so it is not strictly possible to compare these results with those of Steacie et al. whose highest contact time was 0.568 second. However, no increase in velocity constant with time of contact was observed from these results, shown

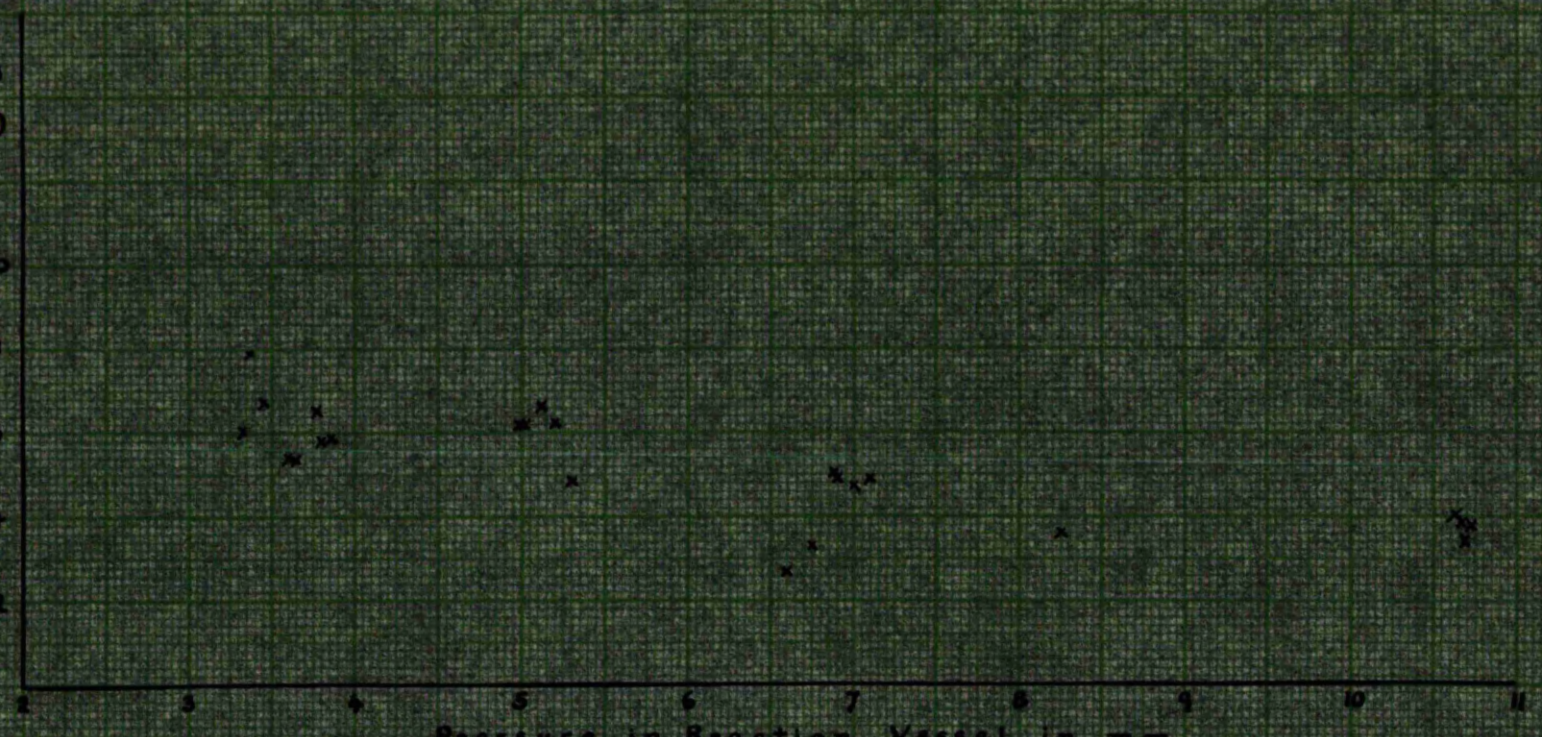
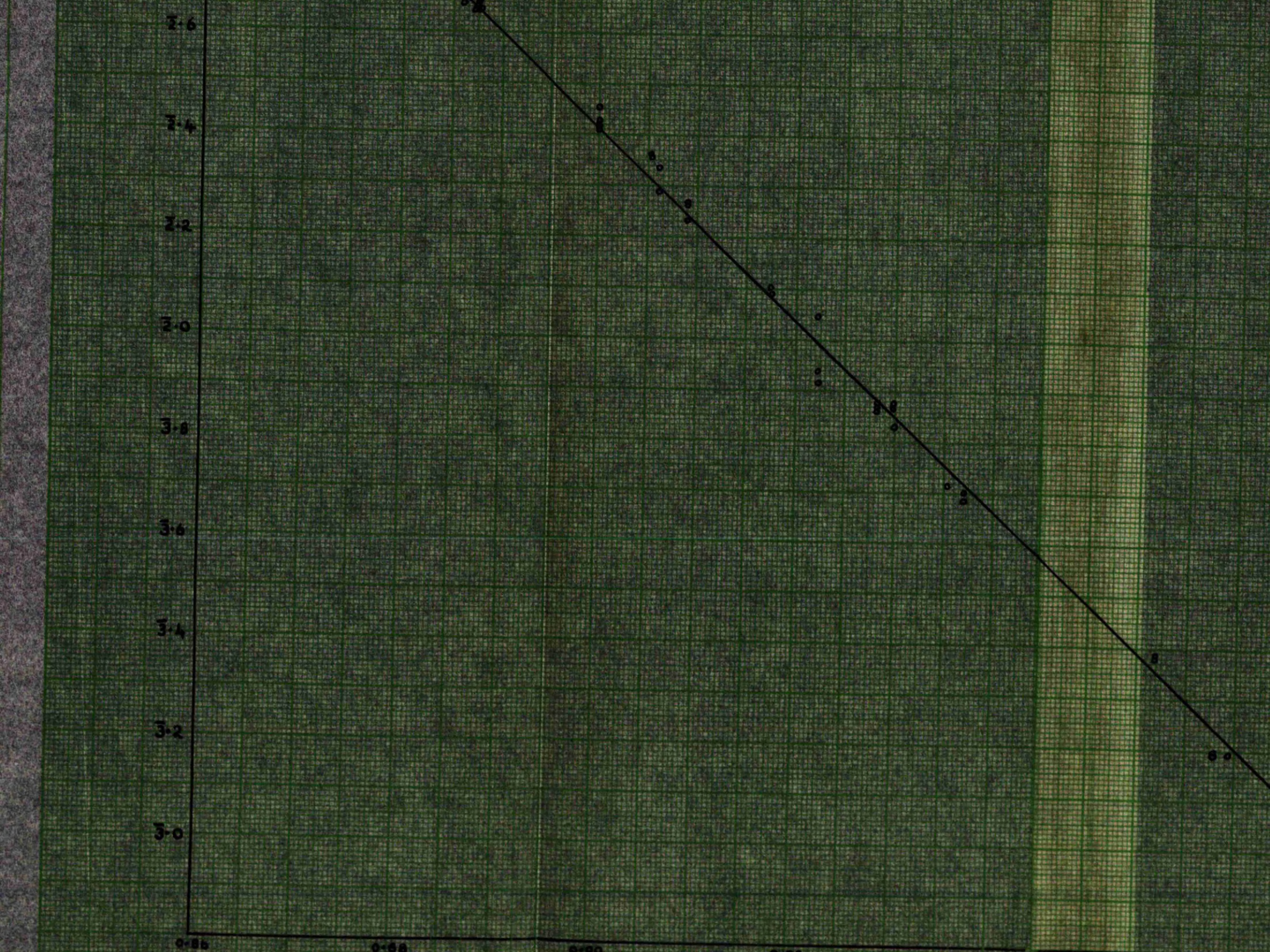

k x 10^3 (sec^-1)
10
8
6
4
2
2
3
4
5
6
7
8
9
10
11
Pressure in Reaction Vessel in m.m.

FIGURE (33).

in Fig.(32), and it is possible that the decrease observed by Steacie et al. at low times of contact, 0.068 to 0.319 second, was due to the toluene not reaching the temperature of the reaction vessel.

Since it had been observed that more reproducible results were obtained when higher pressures of the carrier gas were used, some decompositions were carried out with varying pressures of nitrogen, with times of contact in the region 0.83 ± 0.13 second, and partial pressures of toluene in the range 1.56 ± 0.20 mm. The results are shown in Fig.(33), and indicate that there is a decrease in the rate of about 33% with a three to four-fold rise in the total gas pressure, but this effect appears to cease at about 7 mm. total pressure. This would suggest that at the lower pressures a faster reaction can take place at the wall.

The remaining topic to be investigated was the temperature dependence of the velocity constant, and the reaction was carried out over the temperature range 772 to 880°C, thus covering the upper and lower parts of Szwarc's and Steacie's work. A graph was drawn with values of log. (first order velocity constant) and $1/T^{\circ}K.$ as variables, Fig.(34), the straight line through the points being drawn by the method of least squares. Values for the parameters in the equation:-


2·6
2·4
2·2
2·0
3·8
3·6
3·4
3·2
3·0
0·85
0·90

$$\log_{10} k = \frac{-E}{2.303RT} + \log_{10} A$$

were calculated from the graph, and found to be:-

$E = 84.7 \pm 1.5$ k.cal./mole

$A = 1.3 \times 10^{15}$ second^{-1}.

EXPERIMENTS ON THE PYROLYSIS OF TOLUENE IN A STATIC SYSTEM.

When investigating the temperature dependence of the first order velocity constant, it was not practicable to perform experiments in the flow system at temperatures below about 770°C., and since it was desirable to obtain data at lower temperatures some work was done using a static system.

The apparatus used was the handling system for solids attached to the mass spectrometer, see Fig.(25), and consisted of an injection valve connected to a pyrex reaction vessel, which was enclosed by an electrically heated furnace. Since the proposed furnace temperatures were in the region 700 - 750°C., a pyrex vessel was not suitable, and it was replaced by a two litre silica bulb. The contents of this bulb could be circulated over the mass spectrometer leak, see page 91., so that direct analyses for reactant and products were possible.

The general procedure for the experiments was as follows. The mass spectrometer was prepared for use, and the whole apparatus evacuated. The reservoir on the injection valve was filled with toluene, this was thoroughly de-gassed, and then surrounded by a water bath at about 0°C. Before injecting the toluene, background voltages for the peaks at m/e = 2^+,

15^+, 16^+, 28^+, 91^+, 92^+, 150^+ - 154^+, 163^+ - 169^+ and 176^+ - 183^+ were recorded. In order to have a measure of the sensitivity of the instrument, a known pressure of nitrogen was injected through the leak in the gas handling system at the same time as the toluene was being decomposed, and the voltage of the peak m/e = 28^+ was recorded at intervals throughout the experiment.

The decrease in the toluene concentration was followed by measurements of the peaks m/e = 91^+ and 92^+, and the hydrogen and methane produced observed by the increase of the voltages at m/e = 2^+ and 16^+, the voltages being recorded at known times. As it was of interest to know whether the products at these lower temperatures included any diphenyl compounds, a scan over the peaks in the regions m/e = 150^+ - 154^+, 163^+ - 169^+ and 176^+ - 183^+ was also taken. The temperature of the reaction vessel was noted, and the pyrolysis continued for approximately two hours.

The investigation of the reaction in the static system was limited to a few experiments. This was due to the preliminary work showing that further complications existed at high percentages of reaction, and that the furnace elements and lining would need to be re-designed for further service. The following points were noted, however. Using

an initial pressure of toluene of 7.85 mm., and a temperature of 750°C., and plotting separately against time, the decay of the toluene and the rise of the hydrogen and methane concentrations, it was possible to obtain initial rates of reaction from the slopes of the tangents to the curves. Velocity constants based on this type of data are marked 'S' on Fig. (34), and seem in general agreement with the extrapolated line through the flow data at higher temperatures.

The ratio of the initial rates of hydrogen to methane formation gave a value of 72.8 : 27.2 in agreement with the flow data. By continuing the reaction, however, it was found that the eventual gas composition was nearly equimolar in hydrogen and methane, and in one experiment, 0.8 moles of hydrogen and 0.8 moles of methane per mole of toluene were observed after a long period. From stoichiometric considerations this leaves a residue which is largely carbon, and the reactor was indeed coated visibly with carbon.

The mass spectrum from m/e = 150^+ to 182^+ showed the same character in the early stages of the reaction as observed for the solid products from the flow system. This is of distinct interest as it shows that diphenyl type compounds are formed even at temperatures much lower (100°) than those used by Steacie[6]. A peak at m/e = 178^+ was also noted, indicating the probable formation of anthracene or phenanthrene in addition

to the diphenyl compounds.

Mr. J. L. Rhind has continued this work in St. Andrews with a more heat resistant furnace, and confirms the general conclusions above. In particular, at 730°C. he found an initial hydrogen to methane ratio of 71.4 : 28.6, and observes a carbon coating removable as carbon dioxide. The author is indebted to him for this information.

D I S C U S S I O N.

Before attempting to interpret the kinetic parameters of any process, it is essential to have a soundly based knowledge of the materials formed, because it is from these data and the kinetic laws which have been elucidated that possible reaction paths can be inferred. In his original work, Szwarc[1] simplified the picture of the toluene pyrolysis by inadequate examination of the products, and was able to advance a mechanism arising from an initial dissociation:-

$$C_6H_5CH_3 = C_6H_5CH_2\text{-} + H\text{-} \qquad (1)$$

followed by:-

$$H\text{-} + C_6H_5CH_3 = C_6H_5CH_2\text{-} + H_2 \qquad (2)$$

$$H\text{-} + C_6H_5CH_3 = C_6H_6 + CH_3\text{-} \qquad (3)$$

or:-

$$CH_3\text{-} + C_6H_5CH_3 = C_6H_5CH_2\text{-} + CH_4 \qquad (4)$$

with final removal of benzyl radicals as dibenzyl,

$$2\ C_6H_5CH_2\text{-} = C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$

This interpretation with reaction (1) as the rate determining step and an activation energy as low as 77.5 k.cal./mole seemed more convincing than any scheme requiring:-

$$C_6H_5CH_3 = C_6H_5\text{-} + CH_3\text{-} \qquad (6)$$

Even with the values of the heats of formation of radicals available at that time, it was probable that process (6) was about 90 k.cal./mole endothermic. Activation energies which

are lower than the endothermicity of the primary step occur as a result of chain reactions, but the only chain route to explain the products would seem to be formed from steps (1), (2), (3), (4) and (7),

$$C_6H_5CH_2 + C_6H_5CH_3 = (C_6H_5CH_2-)_2 + H- \quad (7)$$

This last step seemed unlikely as it would have a high activation energy.

In succeeding years, Szwarc, by application of his toluene carrier gas technique, added to the number of reactions where he claimed first order dissociations to be rate determining steps, where temperature independent factors were always found to be close to 10^{13}, and where benzyl radicals always dimerised.[2,3,4,22]

This buttressing of the mechanism for the pyrolysis of toluene has to be examined with reference to the main postulates. There seems to be no doubt from the results of this work and that of Steacie et al.[6] that the products of decomposition of toluene contain materials which cannot be fitted into Szwarc's mechanism with ease. Szwarc's justifiable comment that Steacie's higher experimental temperatures might have caused side reactions to produce diphenyl compounds cannot, in fact, be supported by the data of this thesis. The present work took place within the same temperature range as his own, and the analyses given earlier show the presence of substantial amounts of dimethyldiphenyls, some monomethyldiphenyls or diphenylmethane, a little

diphenyl, some ethane and ethylene, in addition to the materials he specified.

It is not impossible to devise methods for the production of these substances which follow the initial dissociation (1) postulated. For example if:-

$$H\text{-} + C_6H_5CH_3 = C_6H_5\text{-} + CH_4 \qquad (8)$$

is assumed in addition to (3), then diphenyl and diphenylmethane are easily produced. The methyl radicals produced in (3) can lead to some ethane, which under radical attack, gives ethylene. If hydrogen abstraction from the ring is also included as in

$$H\text{-} + C_6H_5CH_3 = H_2 + \text{-}C_6H_4CH_3 \qquad (9a)$$

$$C_6H_5\text{-} + C_6H_5CH_3 = C_6H_6 + \text{-}C_6H_4CH_3 \qquad (9b)$$

$$CH_3\text{-} + C_6H_5CH_3 = CH_4 + \text{-}C_6H_4CH_3 \qquad (9c)$$

we have all the necessary complications to describe the products. Any arguments against them have to be based on their probable rates under the experimental conditions. Excluding (6) and (7), this gives seven separate reactions to produce the products we have shown to exist. Some economy of steps can be obtained if the simultaneous occurrence of (1) and (6) is assumed. This would eliminate the need for (3) and (8). However, Steacie's demonstration[20] that hydrogen atoms produced from decomposing propylbenzene attack $C_6H_5CD_3$ and result in the formation of CD_3H, and our finding of an enhanced methane production from

experiments with toluene and fluorene mixtures both confirm (3) or (8) to be possible reactions.

The experimental work with deuterium as carrier gas adds some useful qualitative points which have to be incorporated in any satisfactory scheme. The data obtained show a marked increase in the rate of methane production (page 122), while the methane, the unchanged reactant and the benzene formed were all deuterated. A simple explanation of the increased methane could be given by the sequence:-

$$C_6H_5CH_3 \rightleftharpoons C_6H_5\text{-} + \text{-}CH_3 \qquad (6)$$

$$CH_3\text{-} + D_2 = CH_3D + D\text{-} \qquad (10)$$

In this mechanism, reaction (10) would be providing an alternative method for the removal of methyl radicals, and when it operated would leave in the system an active entity - a deuterium atom. From the data given earlier, the extra methane production is accounted for to the extent of 80% by the CH_3D formed. There is, however, an objection to this picture. When using nitrogen as a carrier gas, it implies that there is an almost exclusive recombination of about 75% of the methyl and phenyl radicals formed to give toluene. This is very curious in a system containing easily attacked substances such as toluene, and probably a concentration of benzyl radicals which would be higher than that of any other radical species. The attack of radicals on toluene [37,50,51]

is subject to an energy of activation requirement of 7 - 11 k.cal./mole, but at 1100°K., this merely means one in 100 collisions might be effective. Since the toluene concentration was certainly many powers of ten higher than the concentration of any radical, this impediment could not be a determining factor. The fact that ethylbenzene has not been observed as a result of the toluene pyrolysis does not favour combination of benzyl and methyl radicals.

We are not, therefore, inclined to consider that a serious proportion of recombinations of methyl and phenyl radicals exists. Instead of this, it seems better to point out that if reaction (10) is followed by:-

$$D- + C_6H_5CH_3 = C_6H_5D + CH_3- \qquad (11)$$

there is the possibility of some chain steps. Reaction (3) has been established by this work and by Steacie as being operative at these temperatures.

Another noteworthy feature in the experiments with deuterium is the fact that the toluene was deuterated at about three times the rate at which it decomposed - 10% as against 3.7%. Several ways of accounting for this suggest themselves. Of these, the idea of a back reaction:-

$$D- + C_6H_5CH_2- = C_6H_5CH_2D \qquad (12)$$

is not the most convincing. Hydrogen atoms are very reactive and stationary state concentrations are bound to be low, and

this makes the reaction seem unlikely to be so extensive. The possibility of a simple exchange reaction:-

$$D^- + C_7H_8 = C_7H_7D + H^- \qquad (13)$$

would appear to be divisible into separate sections. If the exchange was on the side chain it would presumably involve the usual inversion procedure of the valencies around a carbon atom. This is considered to have an activation energy exceeding 30 k.cal./mole.[52] An alternative process would consider exchange as proceeding by preliminary attachment of the free deuterium atom to the ring system, possibly by the π electron system, and subsequent loss of a hydrogen atom. There is no precise evidence on the rate of such a process but Szwarc[53] has recently claimed that methyl radicals add on to ring systems at ordinary temperatures. Under his conditions he did not observe elimination of hydrogen atoms, and the radical formed was presumed to dimerise or react with the solvent. At higher temperatures decomposition of such radicals becomes more likely, and elimination of a hydrogen atom after addition of the methyl radical is feasible. If this was the mechanism, then it is probable that reaction (3) would pass through a similar transition state before the elimination of a methyl radical. It is obvious that interesting information could be gained if the position of the deuterium - side chain or ring - could have been ascertained.

Attempts to deal with the observed mass spectroscopic cracking pattern of the deuterated material cannot lead to a decision as to the site of the deuterium. This is due to the reasons discussed earlier for believing that the benzyl type ions are really tropylium ions[33] and that all eight hydrogen atoms are indistinguishable for the purposes of mass spectroscopy.

The remaining significant point in the data with deuterium as carrier gas is the proportion of C_2-hydrocarbons to methane in the gaseous products. When using an inert carrier gas the amount of C_2-hydrocarbons was 50 - 100% of the methane formed; when using deuterium this fell to 20%. This is in keeping with the removal of methyl radicals by reaction with the deuterium. The fact that the ethane and ethylene were deuterated can be explained by exchange reactions initiated by attack by deuterium atoms.

The above discussion has only covered the broad qualitative interpretation of the findings on the products of the reaction, and in order to assess the position further, we have to turn to more quantitative considerations. The most important point to decide is whether two bond fission processes occur:-

$$C_6H_5CH_3 = C_6H_5CH_2- + H- \qquad (1)$$

$$C_6H_5CH_3 = C_6H_5- + CH_3- \qquad (6)$$

To do this, the heats of formation of the benzyl, phenyl and

methyl radicals have to be obtained from independent sources and the endothermicity of reactions (1) and (6) calculated.

The data on the heat of formation of the benzyl radical has been described in the introductory survey of the literature. For the present purpose all data on the kinetics of $C_6H_5CH_2$-X compounds obtained by Szwarc have to be eliminated since they are claimed to be consistent with his own findings on toluene. The data of Benson and Buss,[29] Davidson,[24] and Alexander[12] are consistent with reaction (1) having an endothermicity of 84 k.cal./mole, while VanArtsdalen's[5] results require a value of 89.5 k.cal./mole. We propose to adopt $D(C_6H_5CH_2\text{-}H)$ = 84 k.cal./mole since there is greater weight of evidence for this value.

The heat of formation of the methyl radical is known from the work on the bromination of methane,[25] the decomposition of methyl bromide[14] and electron impact data on CH_4 and CH_3-X compounds to be 32.0 k.cal./mole.[30,31] This agreement by several workers is quite satisfactory.

The heat of formation of the phenyl radical is less certain, and a discussion of the relevant data is given in Appendix III. From that discussion, the heat of formation of the phenyl radical is taken to be 72 k.cal./mole.

With these values and the heat of formation of gaseous

toluene we obtain at 25°C.:-

$$D(C_6H_5\text{-}CH_3) = 72 + 32 - 11.95$$
$$= 92 \text{ k.cal./mole.}$$

The data used to derive this quantity are uncertain to an extent which is difficult to assess but cannot be less than $\pm$ 2 k.cal. For accurate comparisons a small correction to this heat of reaction to convert it to pyrolysis temperatures is desirable but this would involve estimated specific heats of radicals, and the general accuracy is not sufficient to warrant this treatment.

Using these values:-

$C_6H_5CH_3 = C_6H_5CH_2\text{-} + H\text{-} - 84$ k.cal./mole (1)

$C_6H_5CH_3 = C_6H_5\text{-} + CH_3\text{-} - 92$ k.cal./mole (6)

we can see that at a temperature of 1100°K., and on the assumption of equal temperature independent factors in the rate equations:-

$$\frac{\text{Rate of reaction (1)}}{\text{Rate of reaction (6)}} = {}_{10}8000/4.57 \times 1100$$
$$= 40 \text{ (approximately).}$$

This is a maximum value for the ratio of the rates of these reactions, and if the value of the heat of formation of the phenyl radical was lower by 3 k.cal. then:-

$$\frac{\text{Rate of reaction (1)}}{\text{Rate of reaction (6)}} = 10^{5000/4.57 \times 1100}$$

$$= 10 \text{ (approximately).}$$

In the data of Szwarc[1], Steacie et al.[6] and Genco et al.[7] the hydrogen production is 1.5 - 2 times the methane produced. In the present work, the ratio is closer to three to one, but if we accept the data for the C_2 hydrocarbon production (Table X), we conclude that the hydrogen atoms and methyl radicals could have been present in approximately equal quantities.

The type of calculation above, while informative where substantial differences in heats of dissociation are involved, is less useful in the present case, due to the assumption of equal temperature independent factors.

It is possible to estimate the temperature independent factors by the following route.

The equilibrium constant for a reaction is related to the velocity constants for the forward and reverse reactions by $K_{eq.} = k_f/k_r$, and if the velocity constants are expressible by a formula $k = A. \exp.^{-E/RT}$ then

$$K_{eq.} = (A_f/A_r) \exp.(E_r - E_f)/RT$$

Also from thermodynamics

$$K_{eq.} = \exp.(\Delta S/R - \Delta H/RT)$$

By equating the temperature independent terms

$$A_f/A_r = \exp.(\Delta S/R)$$

This relationship has been used by Trotman-Dickenson[56,57] and Benson and Buss[28] for free radical reactions by estimating the entropies of free radicals involved in particular reactions.

The reactions we are interested in (1) and (6), both involve entropy increases, being dissociation processes. If Trotman-Dickenson's method for estimating the entropy of the larger radicals R is followed, by allowing for the electron degeneracy in the radical by the addition of 1.4 e.u. to the value of the entropy for RH, at 1100°K.:-

$$C_6H_5CH_3 = C_6H_5CH_2- + H- \qquad (1)$$

$$\Delta S = 1.4 + S_H = 1.4 + 33.9$$

$$= \underline{35.3 \text{ e.u.}}$$

$$C_6H_5CH_3 = C_6H_5- + CH_3- \qquad (6)$$

$$\Delta S = S_{C_6H_6} + S_{CH_4} - S_{C_6H_5CH_3} + 2.8$$

$$\Delta S = 111.61 + 60.9 - 135 + 2.8$$

$$= \underline{40.3}$$

Therefore

$$\Delta S_{(6)} - \Delta S_{(1)} = 5.$$

To proceed further with this comparison, we have to assume one of two things. Either we assume as does Trotman-

Dickenson, that dissociation processes have $A_f = 10^{13}$ sec.$^{-1}$ approximately, and thereby predict differences in the value for A_r for (1) and (6), or we assume with Benson that recombination reactions occur at the calculated collision rate and decide that (1) and (6) would differ in their values of A_f. If quantity of data was to be a guide in our choice, we might take Trotman-Dickenson's view, and leave our considerations as being unfruitful; but his views were determined largely from the results provided by Szwarc, much of which is not extensively investigated. Benson and Buss' assumption agrees with the careful investigations on the dimerisation of methyl[58] and ethyl[59] radicals which show a behaviour close to collision theory calculations.

While in the present state of experimental knowledge there is not much evidence to decide between the options, we favour the view taken by Benson and Buss, and accordingly expect:-

$$(A_f \text{ for (6)}/A_f \text{ for (1)}) = \text{exp.}^{5/2}$$
$$\simeq 12 \text{ approximately.}$$

If such a relationship held then, the rate of (6) would approximate to the rate of (1) in spite of the lower heat of dissociation in the latter reaction.

These considerations are rather speculative in their application, since the number of methyl radicals resulting

from:-

$$C_6H_5CH_3 + H- = C_6H_6 + CH_3- \qquad (3)$$

cannot be assessed. They do assist, however, in countering the view that the magnitude of the dissociation energy is the sole factor to be considered in these cases.

The answer to the previous question as to whether (1) and (6) can have comparable rates, appears to be that it is possible. Since two methods of producing methyl radicals, (3) and (6), exist, and little is known about (3), it is not possible to predict if the (methane/hydrogen) ratio should change with temperature. In this research no definite effect was observed, in agreement with Szwarc and Steacie et al. Genco et al. claim a tendency to produce more hydrogen at higher temperatures.

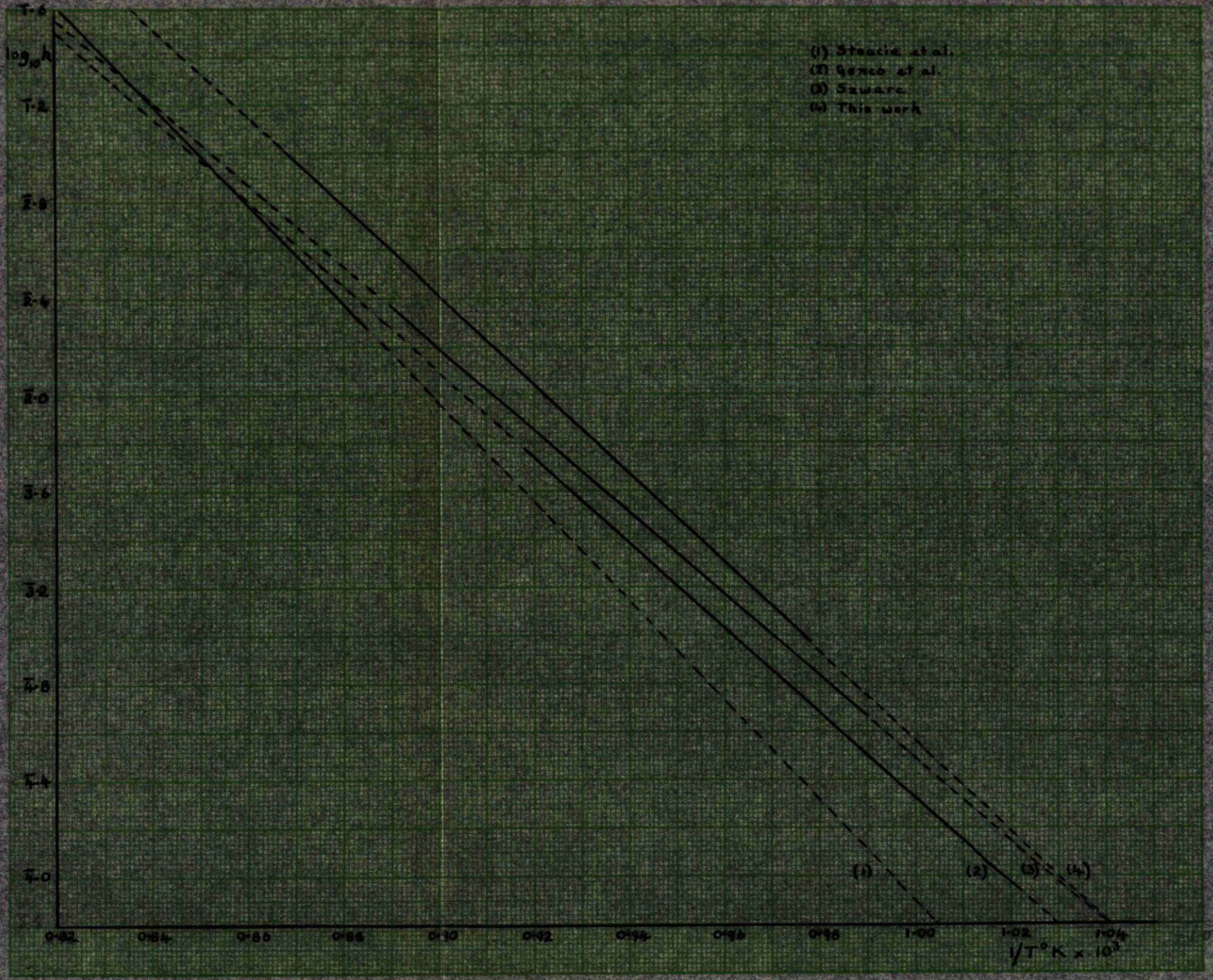
After the above general considerations on the reaction processes, it is convenient to discuss specific features of the experimental findings.

The method of following the production of hydrogen continuously proved that a definite seasoning of the reaction vessel is needed in order to obtain reproducible results. We cannot assert that the final rate achieved was free from a

heterogeneous contribution, but the results showed that variations in reactant pressures did not affect the percentage decomposition significantly at constant contact time, provided that the total gas pressure was greater than about 7 mm. Szwarc claimed that there was no surface effect, while Steacie et al. found the same behaviour as in this work and also used a seasoned reactor for their kinetic data. Genco et al. claimed that a carbonised reactor had no specific catalytic effect.

In previous work, the data defining the order of reaction have not been extensive or obtained with clear separation of the effects of the reaction parameters - contact time and pressure. Examples of Szwarc's data have been given previously (page 9). Steacie et al. considered that the reaction was not first order on the basis of a doubling of the rate with a change in contact time from 0.068 to 0.568 second. This effect could have arisen through lack of thermal equilibrium at the shortest contact times. Their variation of pressure was only from 1.05 to 2.36 cm.Hg. and, like Szwarc's data was accompanied by contact time variations.

The data of this thesis on these topics is much more extensive, and the parameters have been varied separately. The results support a first order law for the reaction.


(1) Stacie et al.
(2) Gence et al.
(3) Szwarc
(4) This work
$\log_{10} k$
$\bar{1}\cdot6$
$\bar{1}\cdot2$
$\bar{2}\cdot8$
$\bar{2}\cdot4$
$\bar{2}\cdot0$
$\bar{3}\cdot6$
$\bar{3}\cdot2$
$\bar{4}\cdot8$
$\bar{4}\cdot4$
$\bar{4}\cdot0$
0·82
0·84
0·86
0·88
0·90
0·92
0·94
0·96
0·98
1·00
1·02
1·04
$1/T°K \times 10^3$
(1)
(2)
(3) ≈ (4)

F I G U R E (35).

The temperature dependence of the deduced first order constants has been given (page 161) as:-

log. k = 15.1 - 84700/4.57 T

and can be compared with Szwarc's data:-

log. k = 13.3 - 77500/4.57 T.

Steacie, while considering his data to be without significance, suggested E = 90 k.cal./mole, while Genco et al. could not decide between 78 k.cal./mole for their data at low temperatures and 84 k.cal./mole at higher temperatures.

Since the separate investigations do not cover the same temperature ranges, Fig.(35) has been constructed, where the data of this research is shown in relation to that of the other workers. The solid lines give the temperature limits of the data. While the present data have velocity constants which are somewhat higher than those from the other sources, it can be seen that the slope obtained is parallel to the line which would be obtained by considering the results of the other three investigations.

Although the data establishing first order kinetic behaviour is better than in previous work, and the heat of dissociation of toluene into a benzyl radical and a hydrogen atom appears from the other data to be close to 85 k.cal./mole, it does not seem to the author that the activation energy can be unequivocally assigned to a bond dissociation energy process.

The products of the reaction have been shown to be complicated and the mechanism is far from clear as a result. It may well be that the rate determining steps are reactions (1) and (6), but the kinetic proof of this is not compelling. In this matter it is easier to believe in postulated mechanisms when the products are simple and the route for their production is quite clear. It is ironical and unfortunate that toluene, which has been widely applied as a reagent to trap radicals and simplify mechanisms cannot act more efficiently and simply in the case of its own pyrolysis.

The observed temperature independent factor $-10^{15.1}-$ is slightly high for a unimolecular bond fission process, where values near 10^{13} have been obtained for many compounds. Values above 10^{13} are known, however, in cases involving the fission of one bond. Such a case is the dissociation of dibenzyl into radicals with $10^{14.3}$ and $10^{15.4}$ in separate investigations,[24,12] others are $10^{14.8}$ in the pyrolysis of benzyl chloride,[60] and $10^{15.7}$ in the pyrolysis of diacetyl.[61]

Reasons for the occurrence of high temperature independent factors can include incorrect kinetic analysis of the order of reaction and chain processes. With regard to the latter, it can be seen from previous pages that it is relatively easy to have chain mechanisms which produce methane but not ones

which produce the main gaseous product hydrogen. The kinetic evidence for first order behaviour from this research is good, and we see little evidence for any chain processes being involved. As a result the value of $10^{15.1}$ is not regarded as being in error due to these causes. It is possible that the use of the (hydrogen + methane) production as an indication of a primary dissociation rate can be in error to some degree, since all the methyl radicals or hydrogen atoms might not always end up in the gaseous compounds. If the products had been simpler this point could have been cleared up.

SUMMARY.

(1) A critical survey of aspects of our knowledge of the heat of formation of the benzyl radical is given in view of its relevance to the heat change in the dissociation process:-

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + H\cdot$$

(2) Previous work on the pyrolysis of toluene by flow techniques is summarised and apparatus devised to study the reaction under more defined conditions with independent variation of reaction time and partial pressure.

Analytical investigations were extended to continuous observation of hydrogen production, and mass spectrometry was applied to identification of gases, liquids and solids.

(3) The existence of the postulated reaction:-

$$H\cdot + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3\cdot$$

has been checked by decomposing toluene and fluorene together in the flow system. The latter substance provides excess hydrogen atoms, and an increase in decomposition was observed.

(4) Decompositions of toluene in the presence of deuterium have shown that products and unchanged reactant all show appreciable deuteration, and it seems that extensive exchange reactions, probably initiated by hydrogen and deuterium atoms,

occur at a rate faster than the decomposition process as judged by (hydrogen + methane) formation.

(5) The products of the reaction not condensible in liquid air averaged 76.7% hydrogen and 23.3% methane. In addition to methane, ethane and ethylene have been shown to be present in appreciable amounts.

The liquid products contained benzene, but not in amount equivalent to the methane and C_2-hydrocarbons found to be present.

The solid products have been shown, by the application of mass spectrometry to a few milligrams of product, to include the following substances in the molar proportions indicated:-

50 - 60 mole percent dibenzyl,

1 - 2 mole percent diphenyl, and the remainder dimethyldiphenyls and monomethyldiphenyls in the ratio 4 : 1.

(6) The kinetic data on the reaction have been obtained within the following range of conditions:-

772 - 880°C;

reaction times 0.565 - 2.076 seconds;

toluene partial pressures 0.56 - 2.34 mm.;

total gas pressure 3.33 - 10.73 mm.

The carrier gases have included nitrogen, helium and deuterium. A small number of experiments in a static system extended the temperature range to 750°C.

(7) It has been shown that, judged by the (hydrogen + methane) production, the reaction was first order over the range of flow system variables indicated in (6). In order to get consistent data 'seasoning' of the reaction vessel was essential, and this process was followed by application of a thermal conductivity gauge method.

(8) The temperature dependence of the first order rate constants was given by $\log_{10} k_{(sec.^{-1})} = -\frac{84700}{2.303RT} + 15.1$.

(9) The results of this work have been compared at relevant points with previous data. It is concluded that Szwarc's views on the simple nature of the processes occurring cannot be maintained. Steacie's criticisms of Szwarc's findings are substantiated even within the latters temperature range of investigation.

It is not felt possible to assert that the experimental activation energy quoted in (8) is the bond dissociation energy for the side chain C-H bond in toluene. It may be the case since it is in agreement with recent independent determinations of the heat of formation of the benzyl radical, but the complexities of the products weaken the case.

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APPENDICES.

APPENDIX I

CALCULATION OF VELOCITY CONSTANTS.

(a) From an Experiment on the Pyrolysis of Fluorene.

Amount of fluorene passed during the experiment which lasted 10 minutes = 2.93×10^{-4} moles.

Amount of hydrogen made = 2.8×10^{-5} moles.

Therefore percentage decomposition

$$= \frac{2.8 \times 10^{-5} \times 100}{2.93 \times 10^{-4}}$$

$$= 9.54\%.$$

The rate of flow of carrier gas obtained from the McLeod gauge readings and corrected by use of the calibration graph, page 49,

= 2.23×10^{-5} moles/second.

Rate of flow of fluorene = $2.93 \times 10^{-4}/600$ moles/second.

= 0.049×10^{-5} moles/second.

Therefore total rate of flow = 2.28×10^{-5} moles/second.

The pressure of gas in

the furnace (page 50) = 6.4 mm.

Furnace temperature = $1072^{o}K$.

$$\text{Time of contact} = \frac{\text{Furnace volume} \times \text{Furnace pressure} \times 273}{\text{Rate of flow in moles/sec.} \times 22400 \times 760 \times \text{Furnace temperature}}$$

$$= \frac{291 \times 6.4 \times 273}{2.28 \times 10^{-5} \times 22400 \times 760 \times 1072}$$

$$= \underline{1.20 \text{ seconds.}}$$

For a first order reaction:-

$$k = \frac{2.303}{\text{Time of contact}} \log. \frac{100}{100 - \% \text{ decomposition}}$$

$$= \frac{2.303}{1.20} \log. \frac{100}{100 - 9.54}$$

$$k = \underline{0.0835 \text{ second}^{-1}.}$$

(b) <u>From an Experiment on the Pyrolysis of Toluene.</u>

Amount of toluene passed during the experiment

which lasted 10 minutes = 8.04×10^{-3} moles.

Total hydrogen made = 4.25×10^{-5} moles.

Total methane made = 1.94×10^{-5} moles.

Total number of moles of

gaseous products = 6.19×10^{-5}

Therefore percentage

decomposition $= \frac{6.19 \times 10^{-5} \times 100}{8.04 \times 10^{-3}}$

$= \underline{0.758 \%.}$

Rate of flow of nitrogen = 2.65×10^{-5} moles/second.

Rate of flow of toluene = $8.04 \times 10^{-3}/600$ moles/second.

= 1.34×10^{-5} moles/second.

Therefore total rate of flow = 3.97×10^{-5} moles/second.

Furnace pressure = 6.8 mm.

Furnace temperature = $1072^{\circ}K$.

Therefore time of contact = $$\frac{291 \times 6.8 \times 273}{3.97 \times 10^{-5} \times 22400 \times 760 \times 1072}$$

= 0.671 second.

For a first order reaction:-

$$k = \frac{2.303}{0.671} \log. \frac{100}{100 - \% \text{ decomposition}}$$

$k = 0.0113 \text{ sec.}^{-1}$

CALCULATION OF RESULTS FROM AN EXPERIMENT ON THE COMBINED PYROLYSIS OF TOLUENE AND FLUORENE.

The data from the combined pyrolysis was used to determine whether an increased quantity of hydrogen or methane was made when the compounds were pyrolysed together. Before each combined run, blank runs on toluene and fluorene were done as described on page 100, and in order to be able to compare data from the blank and combined runs, it was necessary to convert the amounts of products made in the

blank runs to the quantities which would have been made had these runs been performed for the same duration, and with the same time of contact as the combined runs. The method of conversion of the data is shown below:-

(1) Blank Run on Fluorene.

Amount of fluorene passed	= 3.43×10^{-4} moles.
Amount of hydrogen made	= 3.22×10^{-5} moles.
Duration of run	= 10 minutes.
Furnace pressure	= 7.07 mm.
Total rate of flow of N_2 and fluorene	= 2.53×10^{-5} moles/second.

(2) Blank Run on Toluene.

Amount of toluene passed	= 5.74×10^{-3} moles.
Amount of hydrogen made	= 3.19×10^{-5} moles.
Amount of methane made	= 1.32×10^{-5} moles.
Duration of run	= 10 minutes.
Furnace pressure	= 6.62 mm.
Total rate of flow of N_2 and toluene	= 3.11×10^{-5} moles/second.

(3) Combined Run on Toluene and Fluorene.

Amount of toluene passed	= 5.74×10^{-3} moles.
Amount of fluorene passed	= 2.74×10^{-4} moles.
Amount of hydrogen made	= 6.4×10^{-5} moles.
Amount of methane made	= 1.66×10^{-5} moles.

The toluene was passed for 10 minutes and the fluorene for 8 minutes.

Furnace pressure = 6.82 mm.

Total rate of flow of N_2, toluene and fluorene = 3.39×10^{-5} moles/second.

$$\text{Time of contact} = \frac{\text{Furnace volume} \times 273 \times \text{Furnace pressure}}{22400 \times 760 \times \text{Furnace temperature} \times \text{Rate of flow of gases}}$$

$$= \frac{\text{Constant} \times \text{Furnace pressure}}{\text{Rate of flow of gases}}$$

for any set of runs at the same temperature.

In experiments (1), (2) and (3) the times of contact are respectively proportional to:-

$$\frac{7.07}{2.53}, \quad \frac{6.62}{3.11} \quad \text{and} \quad \frac{6.82}{3.39}$$

or to:- 2.79, 2.13, and 2.01.

From (1) the amount of hydrogen made in 8 minutes

$$= \frac{3.22 \times 10^{-5} \times 8 \text{ moles}}{10}$$

$$= 2.58 \times 10^{-5} \text{ moles}$$

For a time of contact proportional to 2.01, the amount of hydrogen which would be made

$$= \frac{2.58 \times 10^{-5} \times 2.01 \text{ moles}}{2.79}$$

$$= 1.86 \times 10^{-5} \text{ moles.}$$

Similarly from (2) for a time of contact proportional to 2.01, the amount of hydrogen which would be made

$$= \frac{3.2 \times 10^{-5} \times 2.01 \text{ moles}}{2.13}$$

$$= 3.02 \times 10^{-5} \text{ moles}$$

And the amount of methane $= \frac{1.32 \times 10^{-5} \times 2.01 \text{ moles}}{2.13}$

$$= 1.25 \times 10^{-5} \text{ moles}$$

Therefore the amount of hydrogen that would be expected in the combined run $= (3.02 + 1.86) \times 10^{-5}$ moles

$$= 4.88 \times 10^{-5} \text{ moles}$$

The amount of methane expected $= 1.25 \times 10^{-5}$ moles

The increase in the amount of hydrogen found over the expected quantity $= (6.4 - 4.88) \times 10^{-5}$ moles

$$= 1.52 \times 10^{-5} \text{ moles}$$

The increase in the amount of methane found over the expected quantity $= (1.66 - 1.25) \times 10^{-5}$ moles

$$= 0.41 \times 10^{-5} \text{ moles}$$

Or the percentage increases are 31.1% for hydrogen and 32.8% for methane.

APPENDIX II.

A. STANDARD MASS SPECTRA.

The data were obtained on the St. Andrews instrument unless it is indicated otherwise, and are quoted as intensities relative to that of the parent or most abundant peak taken as 100.

GASES.

Mass No.	Methane.	Methane. A.P.I.Data.	Methane -d_1 A.P.I.Data.
12	2.41	2.8	2.46
13	7.86	8.1	4.8
14	16.98	16.1	8.8
15	85.50	85.9	20.9
16	100.00	100.0	77.2
17	-	1.11	100.0

Mass No.	Ethane.		Ethylene.	Nitrogen.
25	0.17	(0.56)	11.7	-
26	18.3	(60.6)	62.3	0.10
27	29.2	(96.7)	64.8	0.25
28	100.0	(331.0)	100.0	100.00
29	23.8	(78.8)	2.22	0.75
30	30.2	(100.0)	-	-
31	0.69	(2.29)	-	-

LIQUIDS.

Mass No.	Toluene.	33,62. Toluene	33,62 Toluene - $\propto d_1$	Toluene (A.P.I)	Toluene - $\propto d_1$ (A.P.I.)	Benzene. (A.P.I.)
93	5.5	-	77.4	5.5	84.9	-
92	74.0	67.7	100.0	77.8	100.0	-
91	100.0	100.0	13.3	100.0	26.2	-
79	0.14 (0.144)	-	0.03	0.1	0.7	6.5
78	0.75 (0.957)	0.05	0.66	0.16	0.55	100.0
77	1.47 (1.485)	1.89	1.42	1.17	1.18	14.3
76	- (0.527)	0.61	0.59	0.42	0.55	0.61

SOLIDS.

Mass No.	Dibenzyl.	Stilbene.	Diphenyl-methane.	Fluorene.	Diphenyl.
183	15.16	7.46(?)	-	-	-
182	100.00	58.2 (?)	-	-	-
181	1.99	17.9	-	-	-
180	3.67	100.0	-	-	-
179	5.73	86.6	-	-	-
178	1.59	64.7	-	-	-
169	-	-	13.2	-	-
168	0.4	-	100.0	13.44	-
167	1.1	-	85.7	15.45	-
166	3.45	-	13.8	100.00	-
165	7.83	-	29.4	82.3	-
164	0.85	-	3.52	13.74(?)	-
163	0.65	-	2.52	16.74(?)	-
155	-	-	-	-	8.22
154	0.50	-	1.71	0.09	100.00
153	1.45	-	13.7	0.25	20.3
152	3.7	-	16.3	0.30	16.64
151	1.65	-	1.74	0.10	5.06
92	28.1	-	4.1	-	-
91	440 - 360	-	51.4	-	-
90	5.31	-	4.7	-	-

SOLIDS (contd.)

Mass No.	4-4'-dimethyl diphenyl.	4-Methyl diphenyl.	2-Methyl diphenyl. (A.P.I.)	3-Methyl diphenyl. (A.P.I.)
183	15.6	-	-	-
182	100.0	-	-	-
181	27.7	-	-	-
180	3.17	-	-	-
179	3.05	-	-	-
178	3.53	-	-	-
169	-	14.9	14.1	14.4
168	4.88	100.0	100.0	100.0
167	38.15	52.2	72.3	42.9
166	10.85	11.8	12.8	7.91
165	27.55	28.7	30.4	18.8
164	2.68	4.26	3.31	1.9
163	1.71	4.26	3.01	1.73
155	1.1	-	-	-
154	1.34	-	3.27	1.35
153	3.53	12.77	24.4	11.0
152	7.63	19.15	20.9	16.9
151	1.83	5.32	3.44	2.94
92	1.22	-	-	-
91	9.26	14.9	5.52	5.77
90	4.88	-	-	-

B. MASS SPECTRA OF LIQUID PRODUCTS.

Date & Run.	Volts at m/e = 77^+	Volts at m/e = 78^+	Volts at m/e = 79^+	Volts at m/e = 91^+	Volts at m/e = 92^+	Volts at m/e = 93^+
15.9.56	0.055	0.034	-	3.20	-	-
17.9.56 (1)	0.061	0.064	-	3.40	-	-
(2)	0.102	0.1275	-	5.185	-	-
(3)	0.0925	0.0826	-	4.88	-	-
24.9.56	0.0936	0.0685	-	5.34	-	-
18.9.56 (1)	0.0285	0.047	0.013	1.28	1.035	0.17
(2)	0.018	0.0315	0.007	0.533	0.433	0.068

C. MASS SPECTRA OF SOLID PRODUCTS.

The data are quoted as intensities relative to m/e = 182^+ taken as 100.

Mass No.	Run at 794°C.	Run at 801°C.	Run at 811°C.	Run at 831°C.	Run at 832°C.
183	-	14.05	14.17	10.07	13.7
182	100.0	100.0	100.0	100.0	100.0
181	-	12.5	6.67	7.92	6.52
180	-	9.38	2.5	2.88	3.91
179	-	8.98	4.17	5.9	5.87
178	-	15.63	6.67	6.48	7.82
169	0.65	-	2.5	3.6	2.47
168	4.67	21.1	17.5	25.2	16.95
167	13.05	53.2	35.85	46.2	31.67
166	5.44	21.1	10.0	12.95	9.12
165	12.20	35.15	20.0	25.9	18.9
164	1.38	5.47	-	4.03	1.96
163	1.13	4.68	-	-	1.57
155	-	-	-	-	-
154	-	-	3.32	4.32	5.22
153	1.99	5.87	5.0	5.76	5.61
152	4.83	17.43	9.17	10.07	9.77
151	1.73	4.29	2.5	-	2.61
92	-	19.15	25.0	29.5	31.3
91	-	262.0	338.0	361.0	359.0
90	-	-	5.0	7.2	5.22

C. MASS SPECTRA SPECTRA OF SOLID PRODUCTS (contd.)

Mass No.	Run at 840°C.	Run at 843°C.	Run at 847°C.	Run at 864°C.	Run at 866°C.
183	-	16.0	-	11.5	17.5
182	100.0	100.0	100.0	100.0	100.0
181	-	11.2	-	10.3	19.1
180	-	4.17	-	3.42	8.4
179	-	5.13	-	4.8	8.9
178	-	7.05	-	5.48	11.1
169	4.38	4.0	-	4.97	3.18
168	38.6	33.6	27.35	37.2	48.4
167	90.2	54.8	60.8	85.3	91.3
166	19.2	16.3	17.97	20.4	19.85
165	35.7	29.5	32.8	32.0	46.5
164	4.04	4.53	-	3.61	3.97
163	2.7	2.88	-	2.58	2.38
155	1.31	-	-	1.37	-
154	7.8	4.96	-	7.53	8.26
153	11.7	8.16	4.68	10.6	14.0
152	18.1	12.7	21.35	14.04	23.0
151	4.64	3.2	10.68	3.08	5.56
92	-	-	-	14.96	18.25
91	-	-	281.0	277.0	238.0
90	-	-	-	6.38	11.6

APPENDIX III.

The Heat of Formation of the Phenyl Radical.

The data available for the calculation of this quantity are:-

(1) The bond dissociation energy $D(C_6H_5\text{-}Br) = 71 \pm 2$ k.cal./mole.[63]

(2) The bond dissociation energy $D(C_6H_5\text{-}I) = 60.7$ k.cal/mole.[64]

(3) The bond dissociation energy difference

$$D(C_6H_5\text{-}H) - D(C_6H_5\text{-}I) = 40.5 \pm 1.6 \text{ k.cal./mole.}^{65}$$

In association with these quantities, it is necessary to have the heats of formation of phenyl bromide and phenyl iodide.

(4) The heat of formation of phenyl iodide.

(a) From the same data as (3) above, Ubbelohde et al. obtain from the reaction:-

$$C_6H_5I + HI = C_6H_6 + I_2 \quad \text{that}$$

$$\Delta H_f^\circ \, C_6H_5I_{(g)} = 33.78 \text{ k.cal./mole.}$$

(b) Skinner, Chernick and Wådso[66] quote Lennart-Smith[67] as giving a value for the uncorrected heat of combustion. By making the small corrections necessary for standard state conditions, they obtain:-

$$\Delta H_f^\circ C_6H_5I_{(l)} = 27.6 \pm 1 \text{ k.cal./mole.}$$

Using $\Delta H_{evap.} = 9.6$ k.cal./mole,[68]

$$\Delta H_f^\circ C_6H_5I_{(g)} = 37.2 \text{ k.cal./mole.}$$

(c) From Berthelot's combustion data

$$\Delta H_f^\circ C_6H_5I_{(g)} = 43.1 \text{ k.cal./mole.}$$

This value was calculated by Cowan[64] using modern heats of combustion of carbon and hydrogen.

(5) The heat of formation of phenyl bromide.

(a) From the data of Kablukow and Perelman[69]

$$\Delta H_f^\circ C_6H_5Br_{(l)} = 12.5 \text{ k.cal./mole, and taking}$$

$$\Delta H_f^\circ \text{ evap.} = 9.1 \text{ k.cal./mole}$$

$$\Delta H_f^\circ C_6H_5Br_{(g)} = 21.6 \text{ k.cal./mole.}$$

(b) Smith and Bjellerup[70] obtained a value for

$$\Delta H_f^\circ C_6H_5Br_{(l)} = 8.8 \text{ k.cal./mole leading to}$$

$$\Delta H_f^\circ C_6H_5Br_{(g)} = 17.9 \text{ k.cal./mole.}$$

(6) The difference between the heats of formation of phenyl iodide and phenyl bromide.

(a) Hartley, Pritchard and Skinner[71] measured the heats of bromination and iodination of mercurydiphenyl, and deduced that:-

$$\Delta H_f^\circ C_6H_5I_{(l)} - \Delta H_f^\circ C_6H_5Br_{(l)} = 12.4 \pm 0.95 \text{ k.cal./mole, or}$$

$$\Delta H_f^\circ C_6H_5I_{(g)} - \Delta H_f^\circ C_6H_5Br_{(g)} = 13.0 \pm 1.0 \text{ k.cal./mole.}$$

(b) Some of the data used in their work has been revised[66] as follows:-

$$Hg(C_6H_5)_{2(s)} + 2\ I_{2(s)} = HgI_{2(s)} + 2C_6H_5I_{(l)}$$

$$\Delta H = -37.2 \text{ k.cal./mole.}$$

$$Hg(C_6H_5)_{2(s)} + 2Br_{2(l)} = HgBr_{2(s)} + 2C_6H_5Br_{(l)}$$

$$\Delta H = -78.53 \text{ k.cal./mole.}$$

Using $\Delta H_f^o\ HgI_{2(s)}$ $= -25.2 \pm 0.2$ k.cal./mole

and $\Delta H_f^o\ HgBr_{2(s)}$ $= -40.64 \pm 0.24$ k.cal./mole

we can obtain:-

$\Delta H_f^oC_6H_5I_{(l)} - \Delta H_f^oC_6H_5Br_{(l)} = 12.93$ k.cal./mole

or $\Delta H_f^oC_6H_5I_{(g)} - \Delta H_f^oC_6H_5Br_{(g)} = 13.51$ k.cal./mole.

(7) These data can best be compared by calculating the heat of formation of the phenyl radical:-

(a) From (2) and (4a)

$C_6H_5I = C_6H_5 + I - 60.7$ k.cal./mole.

Therefore:-

$$\Delta H_f^oC_6H_{5(g)} = D(C_6H_5\text{-}I) + \Delta H_f^oC_6H_5I_{(g)} - \Delta H_f^oI_{(g)}$$
$$= 60.7 + 33.78 - 25.48$$
$$= 69.0 \text{ k.cal./mole.}$$

(b) From (2) and (4b)

$$\Delta H_f^oC_6H_{5(g)} = 60.7 + 37.2 - 25.48$$
$$= 72.4 \text{ k.cal./mole.}$$

(c) From (2) and (4c)

$\Delta H_f^\circ C_6H_5{}_{(g)}$ = 60.7 + 43.1 - 25.48

= 78.3 k.cal./mole.

(d) From (1) and (5a)

$\Delta H_f^\circ C_6H_5$ = 71 + 21.6 - 26.7

= 62.2 k.cal./mole.

(e) From (1) and (5b)

$\Delta H_f^\circ C_6H_5$ = 71 + 17.9 - 26.7

= 62.2 k.cal./mole.

The values of $\Delta H_f^\circ C_6H_5$ derived from $\Delta H_f^\circ C_6H_5Br$ and $D(C_6H_5\text{-}Br)$ are low compared with the values from phenyl iodide data, and the data in (6) supplies a method of cross-checking these heats of formation.

Calculating $\Delta H_f^\circ C_6H_5Br$ the values obtained are:-

From (4a) and (6) ΔH_f° = 20.27 k.cal./mole

(4b) and (6) ΔH_f° = 23.7 k.cal./mole

(4c) and (6) ΔH_f° = 29.6 k.cal./mole

Comparing these with the experimental values of 21.6 and 17.9 k.cal./mole, the latter value seems rather low. The data of (6) on $\Delta H_f^\circ C_6H_5I$ - $\Delta H_f^\circ C_6H_5Br$ if taken as true can be altered to $D(C_6H_5Br)$ - $D(C_6H_5\text{-}I)$ thus:-

$$\Delta H_f^\circ C_6H_5I_{(g)} - \Delta H_f^\circ C_6H_5Br_{(g)} = \Delta H_f^\circ C_6H_5 + \Delta H_f^\circ I - D(C_6H_5\text{-}I)$$
$$- \Delta H_f^\circ C_6H_5 - \Delta H_f^\circ Br + D(C_6H_5Br)$$
$$= D(C_6H_5\text{-}Br) - D(C_6H_5\text{-}I) + \Delta H_f^\circ I$$
$$- \Delta H_f^\circ Br$$
$$= D(C_6H_5\text{-}Br) - D(C_6H_5\text{-}I) + 25.48$$
$$- 26.7$$
$$= D(C_6H_5\text{-}Br) - D(C_6H_5\text{-}I) - 1.2$$

The experimental value for $D(C_6H_5\text{-}Br) - D(C_6H_5\text{-}I)$ from (1) and (2) is 10.3 k.cal./mole, making the right hand side of the above equation equal to 9.1 k.cal./mole, whereas Skinner's experimental value (6) is 13.5 k.cal./mole.

If the separate ΔH_f° values for C_6H_5I and C_6H_5Br are taken from (4a), (4b), (4c), (5a), and (5b), and used to obtain $\Delta H_f^\circ C_6H_5I - \Delta H_f^\circ C_6H_5Br$, the situation is confusing due to the number of different values. The lowest difference obtained from this data, however, is (4a) - (5a) = 12.18 k.cal./mole. (Throughout the above, no use has been made of the claimed uncertainties of the data. In view of the spread of values, these uncertainties have more than an optimistic appearance.)

Since $\Delta H_f^\circ C_6H_5I - \Delta H_f^\circ C_6H_5Br$ seems to be higher than the current values of $D(C_6H_5\text{-}Br)$ and $D(C_6H_5\text{-}I)$ suggest, it is possible that one of the latter is wrong. An increase of 4 k.cal./mole in $D(C_6H_5\text{-}Br)$ or a decrease of four in $D(C_6H_5\text{-}I)$

would produce a greater measure of agreement. In the case of C_6H_5I the decrease of four to 56.7 k.cal./mole is not probable. Before Cowan's work, Szwarc tried to decompose C_6H_5I in pyrex vessels, failed, and suggested $D(C_6H_5\text{-}I)$ was greater than 57 k.cal./mole.

Before deciding on a value for $\Delta H_f^\circ C_6H_5$ a further line of argument can be used. The pyrolysis of diphenylmethane[38] has been shown to give $(C_6H_5)_2CH\text{-}$ + H- as the probable first products and not $C_6H_5\text{-}$ + $\text{-}CH_2C_6H_5$. Compounds derived from the latter were not observed, and the energy of activation was found to be 73 k.cal./mole. If this is so, $D(C_6H_5\text{-}CH_2C_6H_5)$ must be greater than 73 k.cal./mole if the two processes:-

$$C_6H_5CH_2C_6H_5 \longrightarrow C_6H_5CH\,C_6H_5 + H \qquad (a)$$

or $$C_6H_5CH_2C_6H_5 \longrightarrow C_6H_5 + CH_2C_6H_5 \qquad (b)$$

are assumed to have the same temperature independent factor. For process (b) not to occur parallel to process (a) to an observable extent, it should have an energy of activation equal to, say 78 or 80 k.cal./mole. If we assume 80 k.cal./mole as the lower conceivable limit of $D(C_6H_5\text{-}CH_2C_6H_5)$, then:-

$$D(C_6H_5\text{-}CH_2C_6H_5) =$$

$$\Delta H_f^\circ C_6H_5 + \Delta H_f^\circ C_6H_5CH_2 - \Delta H_f^\circ C_6H_5CH_2C_6H_5$$

i.e., $$80 = \Delta H_f^\circ C_6H_5 + 37.5 - 33.2 \text{ or } 49.45$$

Therefore, $\Delta H_f^\circ C_6H_5 = 75.7$ or 63.75.

These values are lower limits, and depend on the heat of formation assumed for the benzyl radical. The evidence summarised in the literature survey suggested the best value for $\Delta H_f^\circ C_6H_5CH_2$ is 44 k.cal., which would place $\Delta H_f^\circ C_6H_5$ at not less than 69.2 k.cal.

If we consider this in relation to the various values deduced in (7), we see that (7d) and (7e) are too low to be considered probable; the values in (7a) and (7b) are reasonable, while that in (7c) exceeds the value 75.7 k.cal.

The calculations in (7a), (7b) and (7c) all use $D(C_6H_5\text{-}I) = 60.7$ k.cal./mole rather than $D(C_6H_5\text{-}Br) = 71$ k.cal./mole as the essential primary piece of datum.

From the weight of evidence, we consider that $\Delta H_f^\circ C_6H_5$ may be greater than 69 k.cal./mole, and assume the value 72.4 k.cal./mole. (Skinner et al.[66] concluded that $\Delta H_f^\circ C_6H_5 = 69 \pm 4$ k.cal./mole from some of this evidence.)

APPENDIX IV.

DATA FROM EXPERIMENTS ON THE KINETICS OF THE PYROLYSIS OF TOLUENE.

A. Runs (1) - (58) show the variation of the velocity constant with change in partial pressure of toluene, see Fig.(30), page 157.

Runs (25) - (86) show the variation of the velocity constant with change in the time of contact, see Fig.(32), page 158.

Reaction vessel temperature 802°C.

Date and Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Total H_2+CH_4 Moles x 10^5	Time of Contact sec.	Furnace Pressure mm.	% dec.	k sec.$^{-1}$
1.6.56							
(1)	4.06	1.37	3.08	0.64	7.1	0.758	0.01195
(2)	4.06	1.39	2.95	0.65	7.2	0.726	0.01128
(3)	4.06	1.39	3.15	0.65	7.2	0.777	0.01208
(4)	4.06	1.41	2.82	0.65	7.2	0.694	0.01065
(5)	5.49	1.85	3.56	0.63	6.92	0.648	0.01028
(6)	5.49	1.73	3.49	0.59	7.2	0.637	0.01076
(7)	5.49	1.74	3.29	0.60	7.25	0.599	0.01005
(8)	7.28	2.34	4.33	0.60	7.0	0.594	0.00987
(9)	7.28	2.16	4.02	0.56	7.27	0.553	0.00993
(10)	7.28	2.16	3.96	0.56	7.45	0.543	0.00973
(11)	7.28	2.14	3.81	0.55	7.5	0.523	0.00947
6.6.56							
(12)	2.72	0.60	2.64	0.79	6.65	0.974	0.01247
(13)	2.71	0.62	1.91	0.80	6.52	0.706	0.00883
(14)	2.71	0.62	2.45	0.80	6.46	0.902	0.01132
(15)	2.71	0.61	2.15	0.79	6.6	0.793	0.01014

Date and Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Total H_2+CH_4 Moles x 10^5	Time of Contact sec.	Furnace Pressure mm.	% dec.	k sec.$^{-1}$
7.6.56							
(16)	2.61	0.60	2.93	0.81	6.73	1.124	0.01162
(17)	2.58	0.62	2.18	0.85	6.55	0.844	0.01002
(18)	2.58	0.60	2.33	0.83	6.6	0.904	0.01098
(19)	2.58	0.56	2.56	0.76	6.71	0.859	0.01136
5.6.56							
(20)	1.87	0.63	1.74	0.86	6.87	0.932	0.01168
(21)	1.86	0.61	1.50	0.77	7.03	0.805	0.01047
(22)	1.89	0.63	1.28	0.79	6.87	0.676	0.00859
(23)	1.89	0.63	1.45	0.79	6.8	0.768	0.01006
(24)	1.89	0.62	1.62	0.77	6.8	0.855	0.01115
(25)	2.33	0.92	2.11	0.74	7.0	0.907	0.01240
(26)	2.33	0.94	1.85	0.74	7.0	0.797	0.01077
(27)	2.33	0.92	2.01	0.74	7.0	0.863	0.01180
(28)	2.28	0.92	1.60	0.76	6.87	0.702	0.00924
(29)	2.29	0.94	2.11	0.76	6.8	0.924	0.01223
8.6.56							
(30)	2.85	1.06	2.71	0.90	6.22	0.952	0.01087
(31)	2.85	1.08	2.64	0.89	6.27	0.929	0.01045
(32)	2.85	1.06	2.38	0.88	6.42	0.838	0.00960
(33)	2.76	1.01	2.39	0.86	6.2	0.868	0.01011
(34)	2.76	1.04	2.57	0.89	6.3	0.932	0.01056
(35)	2.76	1.01	2.55	0.87	6.4	0.925	0.01074
12.6.56							
(36)	3.04	0.95	2.87	0.74	6.8	0.945	0.01284
(37)	2.97	0.93	2.54	0.74	6.55	0.855	0.01162
(38)	2.97	0.91	2.71	0.72	6.47	0.910	0.01085
(39)	2.98	0.90	2.82	0.71	6.7	0.947	0.01339
(40)	2.97	0.90	2.71	0.71	6.8	0.910	0.01100
18.6.56							
(41)	4.54	1.10	2.59	0.57	8.07	0.572	0.01005
(42)	4.53	1.11	2.43	0.57	8.15	0.536	0.00937
(43)	4.42	1.12	2.61	0.58	8.15	0.592	0.01024
(44)	4.42	1.09	2.59	0.58	8.02	0.587	0.01019
(45)	4.41	1.10	2.48	0.59	8.1	0.562	0.00961

Date and Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Total H_2+CH_4 Moles x 10^5	Time of Contact sec.	Furnace Pressure mm.	% dec.	k sec.$^{-1}$
19.6.56							
(46)	4.42	1.15	2.93	0.61	8.25	0.663	0.01087
(47)	4.42	1.17	2.63	0.62	8.25	0.596	0.00965
(48)	4.40	1.11	2.69	0.60	8.4	0.611	0.01031
(49)	4.40	1.09	2.39	0.58	8.32	0.544	0.00936
22.6.56							
(50)	4.52	1.11	2.82	0.58	8.07	0.624	0.01086
(51)	4.52	1.09	2.89	0.57	8.2	0.639	0.01134
(52)	4.52	1.10	2.70	0.57	8.3	0.597	0.01048
(53)	4.46	1.09	2.72	0.58	8.25	0.610	0.01065
(54)	4.46	1.09	2.69	0.57	8.3	0.602	0.01055
25.6.56							
(55)	2.48	0.92	2.46	0.90	6.95	0.994	0.01115
(56)	2.51	0.94	2.59	0.89	6.8	1.035	0.01117
(57)	2.50	0.93	2.34	0.87	6.87	0.934	0.01075
(58)	2.50	0.95	2.21	0.90	6.97	0.882	0.00990
(59)	2.50	0.96	2.41	0.90	6.95	0.965	0.01073
(60)	2.50	0.96	2.46	0.91	6.9	0.984	0.01091
13.6.56							
(61)	1.66	0.97	1.68	1.39	7.02	1.011	0.00734
(62)	1.59	0.95	1.51	1.41	6.87	0.950	0.00676
(63)	1.59	0.94	1.67	1.41	6.8	1.049	0.00750
(64)	1.59	0.94	1.74	1.41	7.0	1.094	0.00782
14.6.56							
(65)	1.11	0.82	2.40	1.76	6.88	2.157	0.01238
(66)	1.11	0.82	2.32	1.76	6.92	2.090	0.01200
(67)	1.10	0.81	2.40	1.84	6.9	2.182	0.01199
(68)	1.10	0.83	2.44	1.80	6.87	2.273	0.01195
(69)	1.10	0.79	2.26	1.73	6.9	2.056	0.01201
(70)	1.10	0.80	2.21	1.74	6.92	2.014	0.01170
15.6.56							
(71)	1.11	0.77	1.87	1.64	7.02	1.680	0.01030
(72)	1.11	0.76	1.81	1.62	7.0	1.632	0.01018
(73)	1.11	0.77	2.22	1.65	7.0	1.992	0.01183
(74)	1.11	0.77	1.87	1.65	6.92	1.687	0.01030
(75)	1.11	0.75	1.90	1.61	7.02	1.715	0.01076

Date and Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Total H_2+CH_4 Moles x 10^5	Time of Contact sec.	Furnace Pressure mm.	% dec.	k sec.$^{-1}$
26.6.56							
(76)	1.86	1.01	1.98	1.28	6.5	1.064	0.00837
(77)	1.86	1.05	2.21	1.34	6.8	1.191	0.00898
(78)	1.86	1.01	2.24	1.28	6.85	1.204	0.00945
(79)	1.84	1.03	2.41	1.32	6.8	1.311	0.01000
(80)	1.84	1.14	2.45	1.46	6.87	1.331	0.00920
(81)	1.84	0.94	2.33	1.21	6.9	1.270	0.01060
(82)	1.84	0.92	2.21	1.09	6.95	1.205	0.01114
27.6.56							
(83)	1.41	0.80	2.96	2.08	6.8	2.104	0.01024
(84)	1.40	0.83	2.92	2.10	6.83	2.080	0.01001
(85)	1.40	0.81	2.90	2.06	6.88	2.065	0.01013
(86)	1.40	0.78	2.73	1.99	7.0	1.948	0.00990

B. Variation of the velocity constant with change in total pressure, see Fig.(33), page 160.

Reaction vessel temperature 774°C.

Date and Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Total H_2+CH_4 Moles x 10^5	Time of Contact sec.	Furnace Pressure mm.	% dec.	k.sec.$^{-1}$
3.5.56							
(4)	3.77	1.39	1.67	0.71	5.0	0.443	0.00622
(5)	3.77	1.37	1.75	0.70	5.1	0.465	0.00663
(6)	3.77	1.36	1.65	0.70	5.0	0.437	0.00624
(8)	3.77	1.39	1.76	0.71	3.75	0.467	0.00658
(9)	3.77	1.39	1.57	0.72	3.8	0.416	0.00583
(10)	3.77	1.39	1.50	0.72	3.85	0.398	0.00588
(12)	3.76	1.64	1.57	0.84	7.1	0.417	0.00496
(13)	3.76	1.64	1.51	0.84	7.0	0.402	0.00478
5.5.56							
(3)	3.77	1.43	2.18	0.74	3.33	0.577	0.00605
(4)	3.77	1.42	1.83	0.73	3.35	0.485	0.00794
(5)	3.77	1.42	1.80	0.73	3.43	0.478	0.00667
(7)	3.77	1.47	1.39	0.76	5.21	0.368	0.00634
(8)	3.77	1.47	1.19	0.76	5.29	0.315	0.00488
(10)	3.75	1.78	0.94	0.91	6.6	0.249	0.00275
(11)	3.75	1.70	0.91	0.88	6.6	0.242	0.00276
8.5.56							
(4)	3.56	1.69	1.64	0.91	6.87	0.462	0.00506
(5)	3.56	1.71	1.63	0.92	6.85	0.458	0.00496
(6)	3.52	1.71	1.18	0.94	8.25	0.336	0.00360
(7)	3.53	1.75	1.47	0.96	8.2	0.416	0.00436
(8)	3.53	1.66	1.47	0.91	8.26	0.416	0.00458
(9)	5.05	1.69	2.08	0.97	10.7	0.413	0.00339
(10)	5.05	1.66	1.93	0.95	10.63	0.381	0.00401
(11)	5.05	1.62	1.76	0.92	10.73	0.349	0.00378
(12)	5.05	1.67	1.84	0.96	10.68	0.365	0.00383
11.5.56							
(4)	3.87	1.46	1.51	0.73	3.6	0.391	0.00539
14.5.56							
(5)	3.88	1.50	1.50	0.75	3.52	0.386	0.00518

C. Temperature dependence of the velocity constant
see Fig.(34), page 160.

Date & Run.		Toluene Moles x 10^3	Partial Pressure Toluene mm.	Hydrogen Moles x 10^5	Total H_2+ CH_4 Moles x 10^5
24.7.56	2	1.13	0.91	6.84	8.92
	3	1.14	0.89	7.18	9.36
	4	1.13	0.94	6.39	8.33
	5	1.13	0.92	6.65	8.67
	6	1.13	0.86	6.18	8.06
19.7.56	4	1.67	0.97	7.22	9.34
	7	1.11	0.96	4.69	6.11
23.7.56	2	1.65	1.04	5.74	7.48
	3	1.65	1.04	6.05	7.89
2.8.56	3	1.39	0.97	4.28	5.58
	4	1.39	1.02	4.16	5.42
	5	1.39	1.00	4.02	5.24
	6	1.39	0.96	3.88	5.06
	8	1.39	1.01	4.01	5.23
27.7.56	4	1.68	1.00	4.69	6.11
	5	1.68	1.02	4.69	6.11
	7	1.68	0.95	4.32	5.62
	8	1.68	0.96	4.44	5.78
30.7.56	2	1.40	0.95	3.73	4.86
	4	1.40	1.06	4.05	5.28
	6	1.41	1.10	4.82	6.28
	7	1.41	1.14	3.65	5.99
4.7.56	3	2.11	1.10	4.02	5.24
	4	2.11	0.99	3.94	5.14
	5	2.11	1.04	3.76	4.90
	6	2.11	0.96	3.63	4.73
13.8.56	6	1.40	0.61	1.98	2.58
	7	1.40	0.60	1.93	2.51
14.8.56	5	1.81	0.82	2.51	3.27
24.9.56	4	4.78	1.31	5.37	7.00
3.7.56	4	2.96	1.01	3.26	4.25
	6	2.96	0.96	3.14	4.09
	7	2.96	1.05	3.17	4.13
2.7.56	7	2.87	1.76	2.65	3.45
	8	2.86	1.11	2.43	3.16

Time of Contact. sec.	% decompn.	k sec.$^{-1}$	Temp. ^{o}K.	Date & Run.
0.76	7.86	0.10750	1153	24.7.56 2
0.74	8.22	0.11550	"	3
0.78	7.38	0.09779	"	4
0.77	7.66	0.10390	"	5
0.76	7.16	0.10330	"	6
0.81	5.65	0.07178	1146	19.7.56 4
0.80	5.54	0.07101	"	7
0.88	4.55	0.05298	1137	23.7.56 2
0.88	4.78	0.05594	"	3
0.81	4.00	0.05058	1129	2.8.56 3
0.85	3.90	0.04665	"	4
0.83	3.77	0.04640	"	5
0.80	3.64	0.04634	"	6
0.84	3.76	0.04574	"	8
0.83	3.64	0.04476	1127	27.7.56 4
0.84	3.64	0.04411	"	5
0.78	3.36	0.04377	"	7
0.79	3.45	0.04413	"	8
0.78	3.48	0.04523	"	30.7.56 2
0.88	3.75	0.04371	"	4
0.91	4.45	0.04991	"	6
0.94	4.25	0.04616	"	7
0.96	2.48	0.02605	1111	4.7.56 3
0.87	2.43	0.02834	"	4
0.92	2.32	0.02568	"	5
0.85	2.24	0.02681	"	6
0.81	1.85	0.02294	1105	13.8.56 6
0.80	1.80	0.02280	"	7
0.84	1.81	0.02168	1104	14.8.56 5
0.76	1.46	0.01946	"	24.9.56 4
0.79	1.43	0.01833	1100	3.7.56 4
0.75	1.38	0.01858	"	6
0.82	1.40	0.01708	"	7
0.96	1.20	0.01265	1090	2.7.56 7
0.90	1.10	0.01235	1090	8

Date & Run.	Toluene Moles x 10^3	Partial Pressure Toluene mm.	Hydrogen Moles x 10^5	Total H_2+ CH_4 Moles x 10^5
17.8.56 3	2.85	1.01	2.32	3.03
4	2.85	1.06	2.32	3.03
5	2.86	0.90	2.71	3.53
29.6.56 6	8.23	1.79	2.42	3.15
7	8.23	1.79	2.32	3.02
8	8.23	1.86	2.46	3.21
13.6.56 4	1.66	0.95	1.29	1.68
5	1.59	0.93	1.16	1.51
6	1.59	0.91	1.28	1.67
29.8.56 2	6.08	0.71	2.01	2.63
17.5.56 3	4.06	1.62	1.77	1.83
4	4.06	1.55	1.77	1.83
20.8.56 6	3.75	1.78	0.62	0.81
7	3.75	1.78	0.61	0.80

Time of Contact. sec.	% decompn.	k $sec.^{-1}$	Temp. °K.	Date & Run.
1.24	1.06	0.00861	1084	17.8.56 3
1.31	1.06	0.00818	"	4
1.11	1.24	0.01120	"	5
0.51	0.38	0.00752	1077	29.6.56 6
0.51	0.38	0.00723	"	7
0.53	0.39	0.00737	"	8
1.39	1.01	0.00734	1075	13.6.56 4
1.41	0.95	0.00675	"	5
1.41	1.05	0.00750	"	6
0.84	0.432	0.00517	1069	29.8.56 2
0.91	0.45	0.00500	1067	17.5.56 3
0.94	0.45	0.00480	"	4
0.91	0.22	0.00239	1045	20.8.56 6
0.88	0.21	0.00241	"	7